Colloidal nanocrystal surface chemistry: A perspective based on NMR spectroscopy

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Over the past 20 years, colloidal nanocrystals have emerged as an extremely versatile state of matter. The physical and chemical properties of these hybrid objects depend both on the inorganic core and the ligand-capped surface, with the latter also determining the colloidal stability. Controlling the chemistry of nanocrystal surfaces has proved indispensable for all NC applications, ranging from thermoelectrics and thin-film electronics to electrochromic applications. Among the different methods to investigate nanocrystal surface chemistry, solution NMR spectroscopy stands out as it provides a way second to none to identify and quantify surface-bound ligands.

Starting from an overview of the main techniques in the NMR surface chemistry toolbox, this contribution provides an overview of the current understanding of nanocrystal-ligand binding. Taking the well-known example of metal sulfide and selenide nanocrystals as a starting point, the experimental methodology is introduced and the systematic description of ligand-nanocrystal binding through the covalent bond classification is discussed. Next, the surface chemistry class that characterizes these materials - non-stoichiometry nanocrystals terminated by X-type ligands - is contrasted with ligand binding the lead halide perovskite and metal oxide nanocrystals. It is shown that both types of nanocrystals are terminated by pairs of X-type ligands, a first set binding to Lewis acidic and a second set to Lewis basic surface sites. Finally, taking these two dominant surface chemistries as a reference, the surface chemistry of copper nanocrystals is discussed. The similarities between ligand binding to copper and metal oxide nanocrystals is highlighted, and we conclude that in the case of copper, the nanocrystal-ligand interaction is determined by residual surface oxides rather than the pristine metal.

In conclusion, it is demonstrated that the combination of solution NMR spectroscopy with standard methods for chemical analysis, including mass spectrometry and infrared spectroscopy, can lead to an remarkably detailed description of the nanocrystal surface chemistry. Moreover, the description of the ligand-nanocrystal interaction through binding motifs has created a unified framework that has been successfully applied to semiconductor, metal oxide and metal nanocrystals alike.

Characterization of semiconductor nanocrystals using advanced NMR spectroscopy
Nuclear magnetic resonance (NMR) is one of the most powerful analytical techniques to characterize molecules (solution NMR) and materials (solid-state NMR), including colloidal nanocrystals (NCs). NMR can provide atomistic insights into nature and distribution of species present in NCs, this way shedding light onto the NCs’ composition, chemical dynamics and electronic structure of the NCs. However, NMR is suffering of inherently poor sensitivity, in particular for isotopes other than $^1\text{H}$, $^{13}\text{C}$, $^{19}\text{F}$ and $^{31}\text{P}$. Thus, although most NC materials are constituted of NMR-active elements, they are difficult or not accessible by NMR.

We have presented in earlier work that dynamic nuclear polarization (DNP) is an efficient enhancement technique for NMR signals from NCs, especially for surface-located species, which are particularly low abundant compared to the NC-core atoms. We developed a novel, universally applicable, extremely simple and inexpensive methodology for sample preparation to overcome the low signal intensity. Further, we found 2D-spectroscopy to be an elegant tool to overcome the difficulties of spectra interpretation, by visualizing interactions or by increasing resolution through the isolation of line broadening effects inherent to NCs. (see figure) Eventually, we were often the first to directly observe surface species in NCs. Selectively studying NC-core, NC-surface or capping ligands, may they be of organic or inorganic nature, allowed us to obtain a better understanding of surface processes such as ligand exchange or shell growth reactions onto colloidal semiconductor NCs.
Atomic-level structures of the organic-inorganic interface by NMR crystallography

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Elucidating the binding modes of ligands on nanoparticles is crucial to understand their stabilizing role. Here we show how sensitivity enhancements provided by dynamic nuclear polarization (DNP) allow access to the organic-inorganic interface in a range of technologically relevant nanoparticles and nanocrystals using magic-angle-spinning (MAS) solid-state NMR. In particular we will show how chemical shifts can be used to directly obtain complete three-dimensional structures for organic capping groups in combination with machine learning methods. Notably in the case of gold nanoparticles, we determine the three-dimensional structure, packing and coordination modes of citrate, acetate, succinate and glutarate from carbon-13 and sodium-23 chemical shifts in combination XPS and TEM measurements. In the case of CdSe nanocrystals and CdSe/CdS core/crown nanoplatelets this approach enables the differentiation between surface and core atoms in all major forms of size- and shape-engineered nanoplatelets and their epitaxial nanoheterostructures. NMR signals are assigned to specific crystal facets of oleate-terminated ZB structured CdSe NCs, and interpreted in terms of the surface structures.

Ligand and surfactant distribution on inorganic nanoparticles

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The properties of nanomaterials are largely dependent on the size and morphology of nanoparticles, as well as on their organization within nanostructured materials. A large number of synthetic methods have been developed, which allow an exquisite degree of control over these parameters. One of the most important factors behind particle growth and interparticle interactions is the chemical composition of the nanoparticles’ surface, which often involves the presence of organic ligands, usually surfactants or polymers. These ligands can be used to protect specific crystallographic facets in nanocrystals, to facilitate binding to other molecules or surfaces, but also to direct the assembly of the nanoparticles into well-defined nanostructures. This lecture will provide an overview of the importance of the distribution of organic ligands toward nanocrystal growth and manipulation. Insights will also be provided on the advanced characterization of ligand distribution on nanocrystal surfaces, toward evaluation of Janus nanoparticles.
X-ray-mediated release of molecules and engineered proteins from nanostructure surfaces

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Many applications call for initiation of chemical reactions with highly penetrating X-rays with nanometer precision and little damage to the surroundings, which is difficult to realize because of low interaction cross-sections between hard X-rays and organic matters. Here, we demonstrate that a combination of computational protein design of single conjugation site green fluorescent proteins and nanomaterial engineering of silica-covered gold nanoparticles can enhance the release efficiencies of proteins from the surface of nanoparticles. The nanoparticles, to which the proteins are attached through DNA linkers, provide increased X-ray absorption without scavenging radicals, and single conjugation sites allow efficient release of proteins.

COLL 6

Impact of pH on the orientation of antibody adsorbed onto gold nanoparticles

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Novel detection strategies that exploit the unique properties of gold nanoparticles (AuNPs) hold great promise for the advancement of detection technologies that mitigate biological threats and aid in therapeutic development. Central to these emerging techniques is the immobilization of selective recognition elements such as antibodies onto the AuNP surface. Optimization of the loading density and proper orientation of immobilized antibodies is critical to maximize the analytical performance. Recent studies have demonstrated that proteins with cysteine residues adsorb to gold nanoparticles with strong binding affinity. Moreover, localized regions of charge are responsible for the orientation of the immobilized protein. Here, we measure the adsorption dynamics of anti-horseradish peroxidase antibody (anti-HRP) on gold nanoparticles using nanoparticle tracking analysis (NTA). Solution pH is used to alter the charge distribution on the antibody to investigate the impact on adsorption. NTA facilitates in situ measurement of antibody adsorption on AuNP by measuring the increase in hydrodynamic diameter ($D_h$) of the AuNPs as a function of antibody concentration. Adsorption isotherms are modeled by the Hill-modified Langmuir equation to determine the adsorption affinity, protein layer thickness, and binding cooperativity at each pH. Our data show a monolayer of antibody is formed at saturation at each pH; however, the increase in $D_h$ at monolayer coverage is pH-dependent, suggesting differences in antibody orientation. Differences in antibody orientation were further confirmed by an enzyme-mediated assay to quantify the amount of antibody available for antigen binding. Ultimately, these studies describe, in part, our efforts to elucidate the effect of charge on antibody adsorption onto AuNP to maximize antigen-
binding activity of antibody-AuNP conjugates and enhance the performance of biosensing technologies.

**Coll 7**

**Biomimetic self-assembly of functional gold nanoparticles**

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In nature, biological particles, such as virus capsid self-assemblies are inspirational examples for hierarchical self-assembly with exceptional thermodynamic stability. They follow the principle of genetic economy, efficiency, and error-free structure formation using the concept of subunit-based self-assembly. Related self-assembly concepts have been widely explored in supramolecular chemistry using molecular-level building blocks. However, a similar approach using colloidal level building blocks such as inorganic nanoparticles has certain limitations due to challenges in controlling their size, shape, interactions, and stability. In this contribution, we show biomimetic self-assembly of atomically precise gold nanoparticles into hollow capsids and their application potential in advanced drug-delivery systems (Fig. 1).

In this work, we have explored atomically precise noble (Au, Ag) nanoparticles having an exact number of metal atoms and organic ligands. The synthesis and assembly of the particles were carried out under aqueous environment. The self-assembled structures were characterized using high resolution electron microscopy, Cryo-transmission electron tomography, dynamic light scattering (DLS) and small angle X-ray scattering (SAXS). The nanoparticles containing surface functional groups such as carboxylic acid groups (-COOH) offer directional hydrogen bonding under appropriate conditions. The dispersions of nanoparticles upon dialysis allow hydrogen bonding directed assembly into hollow superstructures with an average size of 200 nm (Fig. 1).

This approach allowed us to explore the possibilities to encapsulate poorly water soluble small molecules. In summary, colloidal self-assembly is an actively growing area of research, where nanoparticle self-assembly is one of the key areas. In an analogy to supramolecular chemistry, which has matured to offer a rich toolbox to construct functional structures beyond the individual molecular scale, a challenge would be to develop rational methods for supracolloidal chemistry, i.e., structures beyond the colloidal range using colloidal level building blocks for materials and biomedical applications.
Molecular mechanical characterization of bioinspired catecholamine polymers at interfaces

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In mussels, the adhesive proteins that are instrumental in attachment to wet surfaces are known to contain high levels of 3,4-dihydroxy-L-alanine (DOPA). A number of coatings for controlling surface chemical properties have been inspired by these proteins. Deposition is facile from an aqueous catecholamine solution onto a variety of solid, porous and nanoparticulate metals, ceramics and polymers. The deposited polyphenol films serve as versatile ‘primers’ facilitating secondary modifications of the primer coating such as metallization and covalent grafting of biomolecules and synthetic polymers. These coatings can be exploited for a variety of practical applications, including antibacterial, antioxidant and fouling resistant coatings on medical devices, metal deposition, plasmonic tuning and surface functionalization of nanoparticles. However, the molecular features of these polymers are not well understood, and their mechanical properties are weak. In this talk we will describe single molecule force spectroscopy measurements that are providing new insight into the structure and interfacial behavior of these molecules. The findings may lead to new approaches to improving mechanical properties.

Role of membrane lipid asymmetry in regulating nanoparticle-plasma membrane interactions
Over the past decade, there has been increasing interest in understanding the mechanisms through which engineered nanomaterials (ENM) disrupt the cell plasma membrane. Despite numerous studies using membrane models, the mechanisms of ENM-induced membrane damage have remained elusive, in part because important structural complexities of the plasma membrane have not been captured in membrane models. In particular, membrane asymmetry, the fact that the cell membrane has different lipids on the exofacial leaflet (i.e. looking away from the cytoplasm) compared to the cytofacial leaflet (i.e. looking toward the cytoplasm) has been completely overlooked. The present study focused on the role of plasma membrane lipid asymmetry in regulating ENM-membrane interactions. Specifically, the effects of plain, carboxyl-, amine-, and polyethylene glycol(PEG)-modified silica nanoparticles (50 and 100 nm) on the integrity of symmetric vesicles, mimicking the exofacial ($V_{exo}$) and cytofacial leaflets ($V_{cyto}$) of the plasma membrane of erythrocytes, asymmetric vesicles, and erythrocyte cells was examined. Nanoparticle interactions with $V_{exo}$ and $V_{cyto}$ vesicles were drastically different. $V_{exo}$ vesicles showed significant leakage after exposure to plain and amine-modified particles, but were not disrupted by carboxyl-modified and PEGylated particles. Conversely, none of the particles caused leakage in $V_{cyto}$ vesicles. In agreement, Forster resonance electron transfer experiments and imaging of giant unilamellar vesicles (GUVs) revealed significant localization of plain and amine-modified particles, but not carboxyl-modified and PEGylated particles, at the surface of the $V_{exo}$ vesicles while only minor localization with the $V_{cyto}$ vesicles was observed for all particles. Importantly, ENM-induced leakage in symmetric and asymmetric vesicles with similar outer leaflet, but different inner leaflet, lipid compositions was similar. In addition, ENMs that induced leakage in $V_{exo}$ vesicles also induced hemolysis in erythrocytes. Taken together, these results suggest that the exofacial leaflet is the primary regulator of ENM-induced leakage with little to no contribution from the cytofacial leaflet.

### COLL 10

**Functionalizing silk fibroin with fluorocarbons via F-capping chemistry to create multiuse inks**

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Silk fibroin (herein referred to as silk) is a broadly applicable biologically-derived polymer with customizable mechanical properties and limited foreign body response *in vivo*. The primary structure of silk mainly comprises non-reactive amino acids, including alanine and glycine, rendering it challenging to modify via traditional synthetic approaches. Previously reported methods to chemically modify the side chains on silk
are limited to introducing functional groups to target specific interactions with biomolecules (e.g., cell attachment, protein adsorption). Functionalization strategies that minimize interactions with biomolecules are equally important for implantable device applications, such as preventing bacterial colonization or cell attachment of certain areas of the implant. Such modifications are seldom reported, and the few reports that exist employ spray coating or other physical modifications of solid silk constructs. Because these strategies modify an already formed solid material, they cannot be used to create constructs with homogenous chemistry, nor can be used to pattern specific construct regions—two features that are desirable when creating an implantable biomaterial.

We report a new synthetic approach to chemically-modify silk side chains with fluorocarbon chains. First, the carboxylic acid content of the silk is enhanced via modification of primary alcohol groups on serine, tyrosine, and threonine residues. Carboxylic acids are then conjugated to ethylene diamine via carbodiimide coupling, resulting in enhanced primary amine content. Finally, a hypervalent iodonium salt containing a fluorocarbon component is added to the silk, where fluorocarbon chains are covalently bound to primary amines via an F-capping reaction. Chemically-modified silks are readily soluble in the organic solvent hexafluoroisopropanol, and thus, can easily be cast into films or used to coat existing solid structures. In this talk, we will discuss the versatility of this modification strategy by utilizing hypervalent iodonium salts with varying fluorocarbon chain length. We will present how wettability and surface chemistry change when different fluorocarbon chain lengths are conjugated to silk. Additionally, we will present proof-of-concept performance testing that illustrates the interactions of modified silk materials with biological systems.

**COLL 11**

**Effect of shape on buckling instability of multilayer hydrogel microcapsules in solutions**

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The majority of naturally occurring micro- and nano-sized particles, such as viruses, cells, and bacteria, have a non-spherical shape, which regulates their biological functions. The ability to create well-defined shaped micro-sized hydrogel matrices can provide a powerful means to regulate shape-dependent particle biodistribution, cellular association, and to optimize drug delivery carriers. Herein, we explored the synthesis and stability of non-spherical pH-sensitive hydrogel microcapsules against osmotic pressure-induced buckling in solution. The multilayer hydrogel microcapsules were synthesized via multilayer assembly of poly(methacrylic acid) (PMAA) and poly(N-vinylpyrrolidone) on spherical (silica) and non-spherical sacrificial inorganic
microparticles of manganese carbonate (cubical), and zif-8 metal-organic framework (rhombic dodecahedral), followed by chemical crosslinking of the poly(acid) layers with ethylenediamine and dissolution of the inorganic templates. The shape and size of non-spherical PMAA hydrogel capsules of varied shell thickness in the solution of different pH values were examined using confocal laser scanning microscopy (CLSM) while scanning electron microscopy was used to confirm complete core dissolution. The atomic force microscopy analysis was used to explore the PMAA hydrogel wall thickness of the hydrogel capsules of spherical, cubical and dodecahedral shapes. We discuss the effect of the hydrogel shell thickness and crosslink density on the maintenance of the capsule non-spherical shape in solution at various pH values. We also discuss deformation behavior of these non-spherical hydrogel capsules in solution with the capsule inward buckling induced by osmotic pressure from fluorescently-labeled poly(styrene sulfonate) sodium salt molecules as studied using CLSM. The knowledge on the shape-dependent deformation behavior of non-spherical hydrogel capsules can provide new insights into the development of advanced drug delivery carriers.

COLL 12

pH-Driven hierarchical assembly of DNA origami nanostructures

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Nowadays the development of DNA origami nanotechnology has advanced tremendous applications in materials science, and bionanotechnology. For example, DNA origami nanostructures have shown their great abilities to organize nanomaterials through their high level of spatial addressability, as well as their potential to integrate with lithographically fabricated substrates, leading to a new generation of electronic circuits. However, to expand the capabilities of DNA origami, a major challenge that needs to be overcome is how to controllably scale-up the size and complexity of DNA origami structures. Recently, different types of environmentally-responsive triggers, such as pH, metal-ion, and light, have been exploited for controlled construction of DNA origami nanoclusters which have demonstrated potential in dynamic, and multi-scale sensing/controlling systems. Nevertheless, the majority of dynamic association/dissociation processes have been controlled by a two-state conversion. To the best of our knowledge, the hierarchical assembly of larger DNA origami nanostructures (> 5 units) with multi-step responsive stimulation has not yet been reported.

Herein, we demonstrate the hierarchical self-assembly of DNA origami multiple-tile nanoclusters via pH stimulation. The cross-shaped DNA origami with pH-sensitive components was fabricated by introducing triplex oligonucleotides on the edges. At pH = 6, the two designed DNA triplexes form triple helices (one strand bound to a B-form DNA double helix through hoogsteen hydrogen bonds). By increasing the pH value, partially unwound DNA could form a bridge with another complementary ssDNA. We
employed this strategy to hierarchically and selectively assemble DNA origami that could grow from a single unit to five units and further to nine units. This process is reversible upon decreasing the pH value. The ordered assembly and disassembly are demonstrated by AFM images and gel analysis. The pH-driven assembly of DNA origami nanostructures in nano-/micro-scale could be potentially utilized in many biomedical fields such as drug delivery systems and nano bio-robots.

**COLL 13**

**Single-step synthesis of alginate microbeads with a PEG shell: A new way to protect encapsulated cells**

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Microbeads of biopolymers such as alginate are widely used to encapsulate cells and other biological payloads. Alginate is attractive because gel beads are easily created by contacting aqueous droplets of sodium alginate with divalent cations such as Ca²⁺. In the gel state, Ca²⁺ ions create ionic crosslinks between alginate chains. However, when alginate gel beads are placed in buffer, the Ca²⁺ ions get exchanged with Na⁺ ions, thereby weakening the gels (due to elimination of crosslinks). Moreover, this causes the gels to swell appreciably and ultimately degrade over time. Consequently, payloads such as cells encapsulated in alginate beads can get released into the external solution, which makes the beads unsuitable for long-term use.

Here, we describe a simple solution to the above problem, which involves forming alginate microbeads surrounded by a thin layer of a covalently crosslinked gel. The layer is formed via free-radical polymerization using conventional monomers such as acrylamide or acrylate derivatives, including PEG-diacrylate. The entire process is performed in a single step at room temperature under mild, aqueous conditions. It involves combining the alginate solution with an initiator, which is then introduced as droplets into a reservoir containing Ca²⁺ and monomers. The droplets are converted into alginate-polymer microbeads within minutes of incubation in the reservoir. Systematic comparisons between these hybrid microbeads and conventional alginate/Ca²⁺ microbeads will be presented. The latter swell and burst when placed in hypotonic solutions or in chelators like sodium citrate, whereas the former remain stable under all conditions. We also show that a variety of human cells can be safely encapsulated in these hybrid beads and that the cells remain viable over long time periods.

**COLL 14**
Fluorescent artificial lipoprotein with improved thermal stability for cell imaging and drug delivery

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Here we report a novel kind of single protein nanoparticles which has a central protein core surrounded by two layers of lipid, one layer of which was covalently attached, and the other layer was physically assembled. The first layer of lipid was attached on the protein via EDC chemistry, in the presence of excess lipid. After the chemistry reaction completed, the extra lipid physically attached on modified protein by self-assembly. These nanoparticles are negatively charged due to the reaction on amine groups and the addition of carboxyl groups. These particles retained the structure of the protein embedded at the core of the particle, but the particles have better thermal stability and a longer shelf time than the constituent protein. These nanoparticles retained 80% of the protein secondary structure after steam sterilization at 121 °C for 30 min, while native protein and the physical mixture lost the secondary structure completely. After labeling with specific fluorescent dyes, these particles emit different colors independent of their size, which can be potentially applied for cell imaging. In addition, these nanoparticles have a faster degradation speed than native protein, which has a potential to be used as drug delivery for fast release. These particles are water-soluble, non-toxic, biocompatible and biodegradable, and suitable for biological applications such as cell imaging and drug delivery.

The synthesis of artificial lipoprotein.

COLL 15

Linking the kinetics of calcium carbonate formation and crystallization to the mechanical response of mineralized hydrogels
Marine organisms are known to fine-tune the physical and chemical properties of gel-like environments within their bodies to guide the precipitation of calcium carbonate and synthesize mineralized tissues with sophisticated microstructures. While the three-dimensional polymer network provides sites for nucleation, the pore solution regulates mass transport to the growing mineral phase and contains soluble additives that can further influence the expressed crystalline morphology. Hydrogels serve as versatile biomimetic models to help shed light on the mechanisms exploited by living organisms to direct biomineralization in such gel-like environments. Therefore, hydrogels remain a subject of intense research due to their potential for tissue engineering applications. In this work, we use a novel combination of spectrophotometry, microscopy, spectroscopy and dynamic mechanical analysis to showcase a mineralization pathway for agarose hydrogels that proceeds through the formation of an amorphous calcium carbonate (ACC), which improves the mechanical response of the composite. While the formation of ACC is highly dependent on the properties of the agarose network, the transformation to a crystalline phase is regulated by the dissolution of ACC only. By introducing an inorganic additive, we exert control over the kinetics of ACC formation, its distribution within the hydrogel, and the resulting crystalline morphology. In-situ mechanical testing during the mineralization step reveals an agarose-calcium carbonate composite with desirable mechanical properties such as increased resilience and lower viscous dissipation. Through this work we share insights into the mechanisms that control the formation of calcium carbonate in hydrogels and how they can open new avenues for designing bioinspired mineralized tissues.

COLL 16

One-pot synthesis of hybrid MoS$_2$/graphene nanosheet suspensions in water for bioelectronic and sensing applications

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MoS$_2$ nanosheets have been extensively explored for their potential use in optoelectronics, photodetection and biomedical applications. However, exfoliated MoS$_2$ provides low conductivity and is difficult to efficiently synthesize due to the tendency of the nanosheets to restack. As a solution, researchers have introduced MoS$_2$ to graphene in order to form MoS$_2$/graphene hybrid nanosheets. This has allowed for the marriage of graphene’s high electrical conductivity and optical transparency, to the superior optical absorption properties of exfoliated MoS$_2$ nanosheets. Currently, MoS$_2$/graphene hybrid nanosheets are synthesized in small amounts via difficult, multistep methods. In this context, we report a simple, efficient, environmentally friendly synthesis method to make MoS$_2$/graphene hybrid nanosheets in water, using bovine
serum albumin. The proposed method can be used to synthesize MoS$_2$/graphene hybrids from their bulk powder precursors, on a multigram scale with a near 100% efficiency due to the ability to recycle unused starting material. These hybrid nanosheets have been characterized with transmission electron microscopy, scanning electron microscopy, X-Ray diffraction, Raman spectroscopy, UV-Visible spectroscopy, and photoluminescence spectroscopy. The MoS$_2$/graphene hybrid nanosheets are biophilic and have the potential to be used in bioelectronics devices, glucose or water sensing, antigen detection, substrate detection, as well as photodetection. In addition, this approach has the potential to be a universal approach for simple, efficient synthesis of other transition metal dichalcogenide/graphene hybrid nanosheets in water.

COLL 17

Self-assembly of biomimetic nanoparticles with amyloid proteins: Concept and functions

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Bacterial biofilms represent an essential part of Earth’s ecosystem that can cause multiple ecological, technological and health problems. The environmental resilience and sophisticated organization of biofilms acting like a multicellular organism are enabled by the extracellular matrix (ECM) that creates a protective network of biomolecules around the bacterial community. Current anti-biofilm agents can interfere with ECM production but, being based on small molecules, they can be degraded by bacteria and rapidly diffuse away from biofilms. Both factors severely reduce their efficacy, while their toxicity to higher organisms create additional barriers to their practicality. In the past, we observed semi-selective self-assembly of inorganic nanoparticles (NPs) with a library of proteins that paved the way to their further experimental and computational studies. In this study, we report on the ability of graphene NPs (GNPs) to effectively disperse mature *Staphylococcus aureus* biofilms, interfering with the self-assembly of amyloid fibers - a key structural component of the ECM. Mimicking peptide-binding biomolecules, GNPs form supramolecular complexes with phenol soluble modulin (PSMs), the peptide monomers of amyloid fibers. Experimental and computational results show that GNPs efficiently dock near the N-terminus of the peptide and change the secondary structure of PSM, which disrupts their fibrillation and represents a novel strategy for mitigation of bacterial communities.

COLL 18

Next-generation of quantum dot sensing

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Optical sensing of environmental parameters like pH, ions or sugar becomes an increasingly important topic in nanobiomedical applications. Although many selective fluorescence dyes are already in use, the need for alternatives with higher stability, reliability and ability for parallel detection of various parameters is constantly growing. We will report a novel concept which fulfills these requirements and which is based on extremely stable quantum dot constructs.

COLL 19

Elucidating the nanoparticle-cell interface

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Bio-responsive nanoparticles are of growing importance with potential applications including drug delivery, diagnostics and tissue engineering (1-3). This talk will describe our research on the design of nanoparticles to interact with cells including new imaging based approaches to study these interactions. Several approaches will be presented including our laboratory’s recently developed comprehensive platform for Single Particle Automated Raman Trapping Analysis (SPARTA™) (4). SPARTA™ is able to integrally analyse nanoparticles ranging from synthetic polymer particles to liposomes with high throughput and sensitivity to resolve particle mixtures, obtain detailed compositional spectra of complex particles, track sequential functionalisations, derive particle sizes and monitor the dynamics of click reactions occurring on the nanoparticle surface. The SPARTA platform opens up a wide range of new avenues for nanoparticle research through label-free integral high-throughput single particle analysis, overcoming key limitations in sensitivity and specificity of existing bulk analysis methods.

COLL 20

Harvesting immunogenic cell death-inducing nanocarriers and catalytically active redox-active nanomaterials for nano-enabled breast and pancreas cancer immunotherapy

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In order to reduce the high mortality of pancreatic (PC) and metastatic breast cancer (BC), we developed a chemo-immunotherapy approach that utilizes liposomal or silicasome carriers to simultaneously trigger immunogenic cell death (ICD) and interfere in a regional immune escape pathway. ICD was induced by doxorubicin or oxaliplatin delivery, in addition to co-delivery of a prodrug interfering in a metabolic checkpoint pathway. Intravenous injection of the encapsulated drug combinations dramatically improved the pharmacokinetics and intratumor drug concentrations of the API in orthotopic 4T1 (breast cancer) and KPC (pancreas cancer) tumor models in syngeneic
mice. The induction of ICD resulted in tumor cell uptake and antigen presentation by dendritic cells, inducing the appearance of TILs. The activation of cytotoxic T-cells induced robust tumor cell killing at the primary as well as metastatic tumor sites. This effect was synergistically enhanced by interference in the metabolic checkpoint pathway, with disappearance of Tregs and an increase in CD8+/FOXP3+ T-cell ratios. Not only did the doxorubicin-delivering liposome provide a synergistic anti-tumor response that is superior to a DOX-only liposome, but also demonstrated that the carrier could be effectively combined with PD-1 blocking antibodies to eradicate lung metastases. In addition to triggering the ICD pathway by drug-delivering nanocarriers, it was also possible to use physicochemical stimuli (e.g., redox-active nanomaterials) to trigger anti-tumor immunity by activating the pathways (ER stress, autophagy and nuclear disintegration) that underpin the ICD effect. All considered, the use of a nano-enabled platform allows switching of immunological “cold” to “hot” tumor microenvironments, with response boosting by co-administered immune metabolic adjuvants or checkpoint blocking antibodies.

**COLL 21**

**Nanoengineering of poly(ethylene glycol) particles for stealth and targeting**

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Poly(ethylene glycol) (PEG) has been widely used to functionalize nanoparticles to reduce nonspecific interactions for drug delivery owing to its intrinsic low-fouling properties. However, the molecular weight and grafting density have been shown to directly influence biodistribution and cellular uptake. This presentation will focus on our work on the synthesis of PEG particles solely composed of 8-arm PEG with tunable size and elasticity via a mesoporous silica templating method. It will be demonstrated that the deformability of PEG particles can be tuned to be similar to that of human red blood cells through cross-linking concentration, as assessed using a microfluidic blood capillary model. Moreover, the biodistribution of PEG particles is size-dependent, and PEG particles with a diameter of 110 nm show extended in vivo circulation time (>12 h), with longer blood retention by at least 4-fold at 12 h postinjection when compared with larger PEG particles. In our ongoing work, we are exploring a range of ligands with PEG particles for targeted delivery.

**COLL 22**

**Nanoparticles interaction with viruses**

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In this talk novel approaches to develop antiviral drugs will be presented. Specifically, nanoparticles capable of irreversibly damage viruses will be presented. It will be argued that that the mechanism of action is that of exerting a pressure on the viral shell. This property, combined with the fact that the particles have minimal toxicity to mammalian cells, renders the particles a potential candidate to the first virucidal drug to get approval for medical use. In particular the case of herpes simplex 2 will be discussed. Other effects of nanoparticles on virus stability and infectivity will be presented.

COLL 23

Utilizing meta-analysis to understand the cellular toxicity of quantum dots

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Understanding the relationships between the physicochemical properties of engineered nanomaterials and their toxicity is critical for environmental and health risk analysis. This task is severely confounded by material diversity, heterogeneity of published data, and limited sampling within individual studies. A meta-analytical approach for extracting and analyzing pertinent knowledge from published studies was previously developed to focus on the cellular toxicity of Cd-containing semiconductor quantum dots (QDs). From literature mining of 307 publications, we obtained 1,741 cell viability-related data samples, each with 24 qualitative and quantitative attributes describing the material properties and experimental conditions. Developing and applying random forest regression models to the data showed that toxicity was closely correlated with several QD surface properties including shell material, ligand and surface modifications, diameter, assay type and, of course, cellular exposure time. Following up from that study, a newly developed resource for meta-analysis of nanomaterial toxicity utilizing Bayesian Networks (BNs) was also tested for exploring the cellular toxicity of Cd-containing QDs. Here, the previously extracted dataset was significantly expanded to now include 517 publications comprising 3,028 cell viability data samples and 837 IC50 values. BN-QD toxicity models were developed using both continuous or numerical and categorical attributes. Using these models, the most relevant attributes identified for correlating IC50 to cellular toxicity were similar to that of the previous study and included: _QD diameter, exposure time, surface ligand, shell, assay type, surface modification, and surface charge, and QD concentration_ for the _cell viability_ analysis. Intense data exploration with the BN models further enabled identification of possible multi-parametric association rules for QDs cellular toxicity. This overall approach of integrating quantitative and categorical data provides for interrogating wide-ranging toxicity data in the literature data suggests that meta-analysis can help develop methods for predicting the toxicity of engineered nanomaterials. Moreover, the available
body of evidence for a given nanomaterial can be readily updated as the body of knowledge expands with more studies.

COLL 24

Water-based environmentally benign flame retardant nanocoatings for textiles

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In an effort to impart flame retardant behavior to woven fabrics made from cotton and cotton blends, an environmentally-benign coating method has been developed. One-pot aqueous complexes, containing polyethylenimine (PEI) and poly(sodium phosphate) [PSP] impart self-extinguishing behavior to cotton-containing fabric. Reduction of total heat release, measured with a microscale combustion calorimeter (MCC), is reduced by more than 80% with just 15 wt% added to a woven fabric. An aqueous complex of PEI and ammonium polyphosphate (APP) forms melamine polyphosphate in-situ during exposure to a melamine-containing solution. Nylon-cotton blended fabric was rendered self-extinguishing with less than 20 wt% coating. A wash-durable form of this coating system can be achieved for polyester-cotton fabric by replacing PEI with poly(allyl amine), which has higher pH-stability. The effectiveness of this halogen-free, flame retardant coating is due to condensed phase activity that includes cooling effects and charring. The ease of this coating procedure and the use of more environmentally benign chemicals deposited from aqueous solutions make this an industrially feasible alternative to current treatments for cotton and cotton-based blends. This same water-based coating technology can be used to impart other useful functionality to textiles (e.g. antifouling behavior).

COLL 25

Microencapsulation of flame retardants: A new approach for imparting fire resistance to nylon-cotton fabric blends

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The development of non-toxic and durable flame retardant fabrics using surface treatment methods is of interest for numerous military and civilian applications. However, most approaches reported currently for surface treatments render the fabric stiff and non-breathable. Microencapsulation is an accepted strategy used to incorporate additives onto textiles. Here we present a new approach for encapsulating safer flame retardants and functionalizing them onto Nylon-Cotton (NyCo) fabric. A phosphorous-based flame retardant is encapsulated in a crosslinked network of bio-based polyphenols. The reaction parameters such as concentration of ingredients, reaction time and stirring rate are varied to optimize encapsulation efficiency. The product is characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX), Dynamic Light Scattering (DLS) and FTIR-ATR. The thermal stability and heat release characteristics of these capsules are studied using Thermogravimetric Analysis (TGA) and Pyrolysis Combustion Flow Calorimetry (PCFC) respectively. These microcapsules are coated to the NyCo fabric and further characterization is carried out on coated fabric swatches. Vertical Flame Test (VFT) is used to study the flame retardant properties of coated fabric swatches. This research opens new possibilities for safer and durable flame retardant materials for fabrics using a microencapsulation approach.

COLL 26

Functional, biobased poly(phosphazene) flame-retardant coatings for textiles

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Phosphazene-based hybrid polymers have raised great interest in many different scientific fields due to their excellent thermal properties, biocompatibility and biodegradability. These outstanding features turn polyphosphazenes into one of the most interesting hybrid inorganic-organic materials. Cyclo-matrix type polyphosphazenes can be synthesized by crosslinking of the hexachlorocyclotriphosphazene (HCCP), with bi- or multifunctional alcohols or amines. Cyclo-matrix polyphosphazenes are promising candidates as carriers, adhesives or flame-retardant polymer additives.

Recently we developed a versatile precipitation polycondencation method to synthesize polyphosphazene colloids with variable chemical structure, crosslink density and size. Starting with hexachlorocyclotriphosphazene (HCCP) and different multifunctional amines or phenols crosslinked cyclo-matrix polyphosphazene particles were synthesized.

In this contribution we will focus on synthesis of hybrid colloids based on HCCTP and natural polyphenol tannic acid (TA). We demonstrate that the combination of two reactive building blocks allows flexible control of the chemical structure for hybrid polymer colloids. The influence of varying reagent ratios on the chemical composition and the morphology of the polymer particles was systematically investigated. Obtained hybrid particles were analysed by FTIR spectroscopy, dynamic light scattering, X-ray photoelectron spectroscopy, elemental analysis as well as $^{31}$P MAS NMR. The
optimized synthesis process allows control of the particle size in extremely broad range (from 100 nm to 5 μm), variation of crosslink density, modification of chemical structure and efficient particle transfer into aqueous phase. Obtained polyphosphazene/TA colloids exhibit extraordinary properties like high thermal stability, degradability and reactive surface. Obtained colloids exhibit excellent adhesion to different fibre surfaces and this allows fabrication thin uniform coatings on textiles by simple dip-coating process. The application of polyphosphazene colloids in flame-retardant and antibacterial textile coatings will be discussed.

**COLL 27**

**Functionalized fabrics for chemical protection**

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Currently available chemical protective garments impose a significant burden on the user, hindering water vapor transport and resulting in significant thermal burden. As a result, use duration is restricted and the suitable range of use scenarios is limited. The JSLIST uniform uses a multilayer approach for protection implemented in a format similar to typical garments. The resulting burden on the user is reduced but not eliminated, and protective capabilities are reduced in comparison to the barrier suits. Daily wear, baseline protection, in addition to current options, would be of use for low hazard environments and other low risk conditions. Beyond DoD concerns, daily wear protection would be of utility to first responders who may enter contaminated environments with no prior warning. A previous effort identified the potential of a microwave initiated process for deposition of fluorinated groups on fabrics to produce oleophobic behavior. There is additional ongoing work focused on sorbents and catalysts for capture and/or decomposition of chemical threats. Organosilicate systems have been widely applied in dip and spin coating approaches, typically, on glass and silicon wafers. We have applied catalyst modified organosilicate materials for binding and neutralization of several targets. The microwave deposition technique developed for fabric fluorination, provides a mechanism for application of the organosilicate materials to fabrics. Here, we use the described process in combination with tetraethyorthosilicate to prepare fabrics. They are then treated with the porous sorbents through a dip coating approach. We have modified cotton and cotton/nylon blends using this approach as well as aramid heat-resistant and polyester cleanroom fabrics. Morphological characterization demonstrates the presence of the porous sorbent on the fabric. While the coating has little impact on water vapor transport through the treated fabrics, evaluation of target permeation through the fabric with and without this treatment shows a significant impact on transport of the target across the material. The deposition approach is suitable for use with other fabrics providing amine and hydroxyl groups for modification and can be used in combination with other sol preparations to produce varying functionality. This ongoing effort focuses on optimization of loading
levels and characterization of the materials against additional targets and in additional environments.

**COLL 28**

**Zinc oxide nanoparticles on polypropylene fibers and films: Adhesion and surface segregation**

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Zinc oxide nanoparticles are one of the more reactive metal oxides. Fibers and fabrics functionalized with ZnO are finding various applications that include gas filtration, catalytic degradation of hazardous gases, and chemical sensing. In the present study, various methods of attaching ZnO nanoparticles to polymer fibers and films, especially polypropylene (PP), are studied. The effect of plasma and ozone treatment on the surface chemistry of PP films has been evaluated with X-ray photoelectron spectroscopy and pull-off adhesion measurements using a functionalized atomic force microscope tip. Our studies show that an oxidized PP surface containing carboxylate groups provides a convenient platform for covalently linking ZnO nanoparticles to the polymer surface. An additional method of decorating the surface of PP fibers and films is being explored that involves melt extruding PP blended with a small amount of ZnO nanoparticles (1-3 wt. %). Various methods of inducing the surface segregation of the nanoparticles in these extruded fibers are being investigated. These include annealing in air and partial vacuum or exposing to ozone gas. For low molecular weight PP, these treatments are adequate to induce surface segregation of ZnO nanoparticles from the near surface region. For moderate to high molecular weight PP, annealing and oxidation of the surface is required. These results are explained by chain mobility and changes in the free energy of the PP surface. Possible photocatalytic and chemical sensing applications of the ZnO/PP composite materials are discussed.

**COLL 29**

**Decontamination of toxic organophosphates using metal hydroxide/polymer textiles: Particle aggregation and its effects on material performance**

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Multifunctional textiles are a growing area of research rising from the continued development of nanotechnologies. Electrospinning to create nanofiber (NF) textiles is one of the more promising techniques for fabricating multifunctional textiles because of its simplicity, scalability and the ease by which additional functionalities can be incorporated into the textile. Electrospun NFs have shown interest in chemical protective suites because of the inherent particle protection of the NFs and the ability to impart decontamination properties to the fabric by incorporating an active component. In this work, the metal hydroxide Zr(OH)$_4$, which has been studied extensively for chemical protection, was incorporated into different polymer substrates using electrospinning along with Ti(OH)$_4$ and Ce(OH)$_4$ for comparison. Additionally, the Ti(OH)$_4$ metal hydroxide was incorporated into the polymer NFs using two different methods. First, the Ti(OH)$_4$ was incorporated as a powder during the sol-gel step just as Zr(OH)$_4$ and Ce(OH)$_4$. Second, the Ti(OH)$_4$ was incorporated as a precursor during the sol-gel step and then hydrolyzed to Ti(OH)$_4$. The catalytic activity of these samples was evaluated using the nerve agent simulant methyl paraoxon (DMNP). The results showed that Ce(OH)$_4$ composite samples had the fastest degradation half-lives ($t_{1/2}$) followed by Zr(OH)$_4$ and then Ti(OH)$_4$. Incorporation of the metal hydroxides into NFs improved the activity of the material over the pure powder form due to reduced aggregation of the particles in the NFs. Finally, the composite samples incorporated with Ti(OH)$_4$ via the precursor achieved $t_{1/2}$’s, faster than the Ce(OH)$_4$ composites. The rapid $t_{1/2}$ of composites incorporated with the precursor was discovered to be due to the uniform distribution of Ti(OH)$_4$ particles throughout the polymer substrate resulting in a hydroxyl decorated polymer surface.

**COLL 30**

Aminated polyacrylonitrile fiber coated with Fe$_2$O$_3$ as a high-capacity adsorbent for phosphorus removal

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Removing the phosphorus from water is a significant issue before discharge the wastewater, because excess phosphorus can cause detrimental problems to aquatic environment, such as changing pH level, oxygen depletion, and eutrophication that cause the algae bloom. Various chemical technologies such as ion exchange and precipitations have been studied to make residual phosphorus concentration lower. However, the adsorbents, including metal (hydr)oxides, clays and etc. are difficult to collect after adsorption and polymer adsorbents based on the ion-exchange are sensitive to pH value.
Iron oxides are well known as a likely choice for the chemical treatment of phosphorus in wastewater, due to a high affinity to phosphorus ion and removal efficiency, less dependence on pH level. However, their form should be modified for increasing the applicability in a large-scale system, due to the limitations such as a costly process, the production of a large volume of sludge and associated disposal problems.

In this work, we propose iron oxide covered aminated polyacrylonitrile fiber (APANF@Fe$_2$O$_3$) as an effective and novel adsorbent for removing phosphorus. The polyacrylonitrile fiber (PANF) was optimally aminated considering the decreasing tensile strength and increasing adsorption capacity, and the iron oxide shell around the fiber’s surface was formed with the chelating ligand which was formed by the amination.

The adsorption capacity of the APANF@Fe$_2$O$_3$ was compared with that of the APANF as control sample and it was noticeably higher than that of the APANF over the whole pH range. The APANF@Fe$_2$O$_3$ showed a considerable PO$_4^{3-}$ adsorption amount of ca. 6 mmol g$^{-1}$ at a low pH region (ca. 2–7) and 3 mmol g$^{-1}$ at a high pH region (ca. 8–12). The adsorption data were interpreted with various kinetic and isotherm models. The Langmuir and pseudo-second-order model were best fitted to the experimental data of the phosphate adsorption on APANF@Fe$_2$O$_3$. The results of this study demonstrate that the surface of the fibrous adsorbent was homogenous and the phosphate adsorption behavior of APANF@Fe$_2$O$_3$ followed a simultaneous chemisorption process into the Fe$_2$O$_3$ layers.

**COLL 31**

**Hybrid dual-functional Ag@Au based nanofilms with high sensitivity for in-situ SERS monitoring of catalytic reaction**

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Hybrid dual-functional Ag@Au nanofilms (NFs) consist of 50 nm Ag nanoparticles (NPs) and 5 nm Au thin coating layers, which is deposited by thermal evaluation (TVD). Ag NPs exhibit high sensitivity for surface enhanced Raman scattering (SERS) and Au thin
layers provide catalytic activity based on the nanoparticle-like morphology. We used Rhodamine 6G (R6G) as Raman probe to evaluated SERS sensitivity and chose the reduction of 4-nitrothiophenol (4-NTP) by sodium borohydride (NaBH4) as model reaction to demonstrate catalytic activity of Ag@Au NFs. Deposition of Au thin layers by thermal evaluation avoid galvanized replacement reaction between Ag and Au occurred in wet chemistry synthesizing method directly. This Ag@Au NFs are prepared with a short time, that is relatively efficient. Also, they were stable enough in redox reactions, like H2O2 decomposition, by taken advantage of the inert property of Au.

COLL 32

Degradation studies on organophosphate methyl parathion mediated by silver-titania core-shell nanoparticles

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Highly water-dispersible core-shell Ag@TiO2 nanoparticles were prepared and were shown to be catalytically active for the rapid degradation of the organothiophosphate pesticide methyl parathion (MeP). Formation of the hydrolysis product, p-nitrophenolate was monitored at pH 7.5 and 8.0, using UV-Vis spectroscopy. 31P NMR spectroscopy confirmed that hydrolysis is the predominant pathway for substrate breakdown under non-photocatalytic conditions. We have demonstrated that the unique combination of TiO2 with silver nanoparticles is required for catalytic hydrolysis with good recyclability. This work represents the first example of MeP degradation using TiO2 doped with AgNPs under mild and ambient conditions. Analysis of catalytic data and a proposed dark mechanism for MeP hydrolysis using core-shell Ag@TiO2 nanoparticles are described.

COLL 33

Self-assembled monolayer of 2D metal oxides: Applications in gas sensing

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2D metal oxides are excellent gas sensing materials due to their large specific surface area and highly reactive surface. Most of the 2D-metal-oxide-sensor studies are
conducted on sensing films several hundred nanometers to several microns thick, because controlling particulate film thickness at submicron-level with conventional techniques is challenging. However, thick film sensors often suffer from target gas consumption when being transported within the film, resulting in dampened sensitivity.

To address this issue, we developed a facile self-assembly method, and, for the first time, fabricated sensors composed of only a monolayer of 2D CuO nanosheets. To prepare the monolayer sample, CuO nanosheets dispersed in ethanol was added dropwise in water. The nanosheets then floated at the air-water interface and self-assembled into monolayer film due to their anisotropic hydrophilicity. By repeating this process, thick films composed of multiple layers of CuO nanosheet were also prepared.

From the monolayer sample (t~30nm), we observed excellent sensing performance towards H$_2$S including ppb-level detection limit (<200 ppb), large sensor response (350% at 5 ppm), and short response and recovery time (20/120 sec at 5 ppm). In comparison, much weaker sensor response (180%, 100%), and much longer response and recovery time (50/220 sec, 110/320 sec) were observed for the thick film samples (t~5μm, 10μm), despite that the same sensing materials were applied in all cases. This strong thickness-dependence was attributed to the surface-reaction-coupled diffusion of gases within the lamellar structure of the sensing films. Based on this theory, a numerical simulation for thickness-dependent sensor response was performed, and good matching with the experimental results was obtained.

These results highlight a facile self-assembly method for preparing monolayer of 2D metal oxide, and the huge advantages the monolayer configuration brings to gas sensing application. Moreover, as the first study concerning the influence of sensing film morphology on the sensing performance of 2D metal oxides, the results provide important design guidelines for the future development of high-performance 2D metal oxide sensors.
Hydrophilic/hydrophobic self-converting nanoreactors

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Stable and effective dispersion in the reaction environment is one of the most important properties for metallic nanocatalysts to obtain a higher activity. Up to now, numerous kinds of surfactants and carrier systems have been developed to stabilize nanoparticles in different solvent environments. However, most of these systems are designed for only one or a few of reactive environments with similar polarities. When the solvent of the reaction changes from water to organic environment with low polarity, or vice versa, the stability of the catalytic system is difficult to maintain.

In the present study, we have designed and synthesized a novel nanoreactor using hydrophilic porous SiO₂ as shells and poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-co-2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMPMA-co-PTMA) amphiphilic copolymers as cores. With the changing of the solvent environment from hydrophilic to hydrophobic, the copolymer cores are swollen and the polymer segments pass through the holes on the SiO₂ shells to wrap the nanoreactors. This process allows the self-conversion the surface layer of the nanoreactors from hydrophilic to hydrophobic as shown in Figs. 1a and 1b. In turn, the nanoreactors obtained in this study are easily dispersed and remain stable in almost all common reagents (see Fig 1c-g). Most importantly, by utilizing the polymeric network as template, Au nanoparticles with a diameter of 3 nm and a narrow size distribution can be generated inside the nanoreactors, which exhibit higher catalytic activity than CTAB stabilized Au nanoparticles in different polar solvents environment conditions. Moreover, this approach can be easily extended to other metallic nanoparticles due to the simple synthesis process.
Encoding molecular information to plasmonic gold nanostars for anti-counterfeiting

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In the last decade, scientists started to apply surface-enhanced Raman scattering (SERS) in the development of novel plasmonic anti-counterfeiting materials. This
approach takes advantage of spectroscopic fingerprints thus is less susceptible to fraud. However, the capacity of information, the sensitivity of detection, and stability of these materials still need to be improved. A key step for such improvements is to make novel plasmonic nanostructures with increased SERS enhancement. Herein, we will use star-shaped gold nanoparticles as SERS substrates. These novel gold nanostars have the ability to improve the sensitivity of SERS detection. Also, various molecules could be attached onto the gold nanostars to provide high capacities of information. The encoded molecular information was then successfully decoded using principal component analysis (PCA). Furthermore, the as-synthesized colloidal tags can be further stabilized by introducing coatings on the surface. This anti-counterfeiting method is unique and effective, and the fabricated tags are easy to be processed and meanwhile, extremely hard to be counterfeited. It is expected that these molecular tags will have extensive applications in business, technologies, and safeties.

COLL 36

Constructing transferrable electronics on functionalized graphene

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Ubiquitous sensing is a rapidly emerging field that requires the installation of vast quantities of small, cheap electronic devices on surfaces of all types, including fragile or biological surfaces. Since in many cases, electronics cannot be directly built or processed on these types of surfaces, a method is needed to build these electronic devices and subsequently transfer them onto their target substrates. We have shown that chemically hydrogenated graphene is capable of delaminating cleanly from its substrate while retaining any functional groups it has as well as many delicate physical properties such as magnetic characteristics. This occurs because hydrogenation weakens the van der Waals adhesive force between graphene and its substrate. We further show that electronically active devices, including a graphene ribbon FET and an ammonia gas sensor, can be constructed directly on hydrogenated graphene and transferred to a variety of surfaces with retention of functionality. This transfer is mild, non-toxic, biocompatible, and involves exposing the surface only to water. Transfer techniques like these will be essential for maximizing the deployment of small electronic devices for ubiquitous sensing.

COLL 37

Impact of solvent quality on graphene transfer process: Toward optimizing graphene transfer onto transparent polymer films

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It is well known that polymer-solvent interactions influence local polymer chain conformations. We examined the impact of both polymer conformation and polymer backbone composition on polymer-graphene adhesion, a critical factor within the graphene transfer process. We prepared drop-cast and pressed polymer films and induced different local polymer chain conformations by varying the solvent quality. These conformations were verified using dynamic light scattering and solution small angle X-ray scattering. Using 2D Raman, optical transmittance, atomic force microscopy, and X-ray photoelectron spectroscopy both before and after graphene transfer, we completed extensive film characterization. Additional rheological testing and contact angle measurements provide adhesion energies between the polymer film and graphene surface. Using these data, we quantify the impact of physical polymer properties on graphene-polymer adhesion and provide guidelines to improve adhesion during the graphene transfer process. These results will allow graphene to be transfer to a variety of polymeric films.

**COLL 38**

**Highly stable boron nitride nanotube (BNNT) dispersions and pastes for thin film coatings and fibers**

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As an analogous material to carbon nanotube (CNT), boron nitride nanotube (BNNT) has attracted a growing attention for a decade due to its superb physical properties such as excellent mechanical strength, toughness, high thermal conductivity, electrically insulating property, and biocompatibility. Moreover, extraordinary properties of BNNT over CNT such as high oxidation resistance (stable up to 900°C), high miscibility with some polymer matrices by ionic interaction, piezoelectricity, and high neutron absorptivity are drawing significant attention from the field of material science related to composite materials such as structural composites, nanoscale electrical devices, and aero-space materials for harsh environments. However, highly stable dispersion of BNNTs especially in volatile organic solvents, which should be achieved for fabrication of homogeneous composites, has still been remained unsolved. In this talk, we will introduce a non-covalent functionalization approach in order to efficiently debundle and achieve a good dispersion and high concentration of BNNT in various solvents without any damages on intrinsic properties of BNNTs. The debundling efficiency of the dispersing agents as well as the stability of BNNT dispersion are systematically investigated by UV-Vis spectroscopy, Turbiscan analysis and scanning electron
microscopy (SEM). In order to emphasize the high thermal resistance and mechanical strength of BNNTs, the highly debundled BNNT dispersion is applied in fabrication of thermally regenerable ultrafiltration membranes which can exclude higher than 99.9% of PS latex with about 25 nm in diameter using very small amount of BNNT. Furthermore, high concentration BNNT pastes showing shear-thinning property, which is essential for coating, were prepared with combinations of various solvents and dispersing agents and applied to fabricate BNNT/polymer composite thin films and fibers.

A) a graph showing the outstanding durability of BNNT membrane even in repetitive reuse process (thermal calcination) to remove PS latex (MPDx : areal mass of X mg/cm² BNNT). B) SEM image of BNNT membrane after 10 times of calcination process at 450°C for 6 hr (inlet: optical image of calcined BNNT membrane).

COLL 39

Paper-derived SiC sheet with high-density stacking faults for high-performance electromagnetic wave absorption

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The goal of recycling paper is efficient utilization of cellulose resources. Currently, the most extensive approach for secondary fibers is to recycle as remanufacturing paper. Herein, we report that papers can be used as a carbon template material to synthesize SiC sheet with excellent microwave absorption. The morphology and microstructure of the SiC sheet have been characterized by scanning electron microscope and powder X-ray diffractometer. These characterizations indicate the growth mechanism of SiC sheets is solid phase reaction coexisting with vapor-solid reaction. There are plenty of stacking faults generated in the domain of SiC, which endow SiC sheets with superior
electromagnetic (EM) wave absorption. The lowest reflection loss reaches -22 dB. Effective EM absorption band (RL < -10 dB) covers the frequency range of 12.8-18 GHz with a thickness of 2.2 mm. Our research provides a novel value-added approach for recycling papers and an excellent EM absorber for industrial application.

**COLL 40**

Gate-enhanced photocurrent of (6,5) single-walled carbon nanotube based field effect transistor

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A visible sensing field effect transistor (FET) with a channel length of 100 nm for individual (6,5) single-walled carbon nanotubes (SWCNTs) is fabricated via a selective sorting method using 9,9-dioctyfluorenyl-2,7-diydleybipyridine (PFO-BPy) polymer. The FET of the (6,5) SWCNTs shows p-type behavior with hundreds of on-off ratios and on-state conductivity of 50 ± 4.0 (Ω m)^{-1}. In addition, the photocurrent of the FET of the (6,5) SWCNTs in the visible range increases (maximum 200 times at 620 nm) with higher gate voltage. E_{22} transition and PFO-BPy transition are observed in the FET of the (6,5) SWCNTs without application of a gate voltage. Interestingly, exciton-phonon coupled E_{22} transition due to gate-doping (p-type), which has been reported in photoluminescence and absorption studies, is expected to occur in the photocurrent of the FET at negatively higher gate voltage. In addition, the exciton-phonon coupled E_{22} transition is prominently observable when carrier concentration by gate doping becomes approximately two-hundred sixty times (260 ± 43) larger than carrier concentration without application of a gate voltage. This demonstration would be useful for the development of SWCNT-based visible sensors with gate control in the SWCNT devices.

**COLL 41**

Surface chemistry of metal deposition and atomic layer etching
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Recent advances in understanding the mechanisms of surface reactions for metal deposition and etching will be highlighted. Atomic layer etching of cobalt surfaces will be used as an example of understanding the fundamentals of metal etching mechanisms, and deposition of silver and platinum will be described for potential applications in catalysis, where the control of the deposited metal nanoparticles is extremely important. We will utilize microscopic techniques, including electron microscopy and atomic force microscopy, to follow the morphology of the materials and surfaces. We will utilize surface analytical techniques (including vibrational spectroscopy, X-ray photoelectron spectroscopy, and thermal desorption) to follow the formation and evolution of surface species, and we will supplement these findings with density functional theory computations to understand the mechanisms of surface reactions. A number of misconceptions about the mechanisms of surface dry etching will be investigated and the roadmap for further understanding of these processes will be proposed.

COLL 42

Epitaxial growth and characterization of Ru (0001) supported hexagonal MoN thin films

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Hydrodenitrogenation, a key step in petroleum refinement, proceeds with greater activity and large-chain selectivity on molybdenum-nitride powders than on conventional catalysts, which are alumina-supported, sulfided, Co-Mo or Ni-Mo active sites. Additional evidence suggests that δ- phase hexagonal MoN is most active, but detailed fundamental studies of phase-pure molybdenum nitrides at a scale sufficient to elucidate clear atomic and molecular level mechanistic explanations of previous materials-activity correlations have yet to be undertaken. This work includes the study of growth and characterization of hexagonal Molybdenum nitride thin films. Molybdenum nitride films were grown on Ru (0001) via ion-assisted physical vapor deposition and subsequent annealing and were characterized by X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and Scanning tunneling microscope (STM). The growth and characterization of films is also supported by Density Functional Theory calculations.

COLL 43

Electrochemical control of the thermal stability of atomically thin Ag films on Au(111)

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In previous research completed by Iski et al. and Itaya et al., it was found that through specific electrochemical methods, a silver (Ag) monolayer could be formed on a Au(111) surface in a chloride-rich or chloride-free solution. The electrochemical method used was under potential deposition (UPD) which formed a monolayer from either AgCl or AgClO₄, respectively. In the previous studies, one specific UPD peak was investigated. Through a detailed electrochemical study, we have found that the UPD of Ag on a Au(111) surface can occur at two different underpotentials, one resulting from the reduction of Ag⁺ to the surface and the other resulting from the reduction of a solvated silver halide unit (AgX) to the surface. Furthermore, we have determined that, depending on the potential supplied to the system, the layer formed at the surface can either be thermally stable or unstable up to 1,000 K. The atomic structure of these films can be studied with electrochemical scanning tunneling microscopy (EC-STM), which not only allows for atomic-scale imaging of the surface layer within an electrochemical environment, but also facilitates the taking of cyclic voltammograms (CVs), which can be used to examine the redox behavior of the systems. Through this electrochemical manipulation, the reduction of Ag⁺ to the surface can be investigated in multiple silver halide systems and the thermal stability investigated. Despite many studies on these types of surface layers, very few publications have directly studied the thermal stability of the UPD of Ag on Au(111) using varied silver halide sources. Through STM imaging, the newly modified surface can be imaged and the structure of the Ag monolayer investigated under a liquid layer while holding a constant potential. STM evidence shows that the amount of Ag on the surface is the same regardless of the Ag source used but does change based on application potential. Furthermore, electrochemical studies into these Ag monolayers have led to a better understanding of the properties of these surfaces and the exact nature of the redox chemistry occurring at the relevant potential. Using EC-STM, studies were conducted on how different UPD depositions affect the thermal stability of the system.

COLL 44

Electrochemically generated superhydrophobic meshes for efficient separation of oil from water

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Water pollution especially contributing by the organic contaminations and accidental oil spills is one of the major environmental challenges due to their direct impact on the human and marine life. A superhydrophobic surface was constructed on the surface of the stainless steel mesh which displayed a specific superwettability. The superhydrophobic mesh selectively allows the passage of the oil while repelled the water as it touches the mesh surface. The superhydrophobic surface was achieved by electrochemically coating the copper and oxidizing the copper on the surface of the
mesh in the strong oxidizing medium. Through this, the grassy like microarchitecture of the copper oxide achieved which spread throughout the stainless steel mesh. The surface has become superhydrophobic after interacting with the fatty acid. The surface strongly repelled water which was evident from the high water contact angle >150 degree. The hydrophobic surface integration on the stainless steel mesh was characterized and confirmed by using the XPS, XRD, SEM and the FTIR instrumentation. The separation efficiency for various non-polar solvents from the water was achieved > 99%. The developed hydrophobic mesh can be a valuable addition to the designed material for oil and water separations due to its controlled morphology, efficient performance and cost-effectiveness.

**COLL 45**

**Computational modeling of graphene oxidation**

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We have simulated the dynamics of high temperature oxidation and pit growth on graphene using accelerated kinetic Monte Carlo calculations in combination with a simplified kinetic mechanism. The model incorporates the essential surface processes controlling oxidation, namely dissociative adsorption of oxygen, epoxy diffusion and desorption and CO desorption. The activation energies of these processes are well-known to depend on the coverage, graphene curvature or the presence of other adsorbed species different from oxygen. In order to account for these effects, we have considered these activation energies as free parameters and let them swing within their expected ranges of variability. The results show how the pit growth rate depends on them. More specifically, we find two generic oxidation regimes: for highly mobile adsorbed epoxy groups, the CO production is kinetically limited by the rate of CO desorption from active (edge) sites. In this regime, the coverage is uniform over the whole graphene surface, and equal to the equilibrium value corresponding to the same temperature and pressure in perfect defectless graphene. On the other hand, when the surface diffusion of epoxy groups is severely hampered by, for instance, foreign adsorbed species, the oxidation rate, and therefore pit growth, is limited by the rate of epoxy diffusion. In this regime the coverage is non-uniform close to the pits as a result of the depletion of oxygen on active sites. We have additionally developed a continuun model which represents oxidation and pit growth in the limit of pits with a length scale much larger than the molecular scale (carbon-carbon distance in graphene). The results from both models compare favorably with published experimental work.
Dynamic adsorption of airborne contaminants on graphite

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Recent advances in wettability studies of highly ordered pyrolytic graphite (HOPG) and other graphitic materials have highlighted the influence of adsorbed airborne contaminants on their interfacial properties. Although graphitic carbon materials have long been reviewed as hydrophobic, we and others have shown that such hydrophobicity is due to contamination from the environment. Given its impactful effect on surface sensitive applications, it is of great interest to fully characterize the coverage and chemical nature of the contamination. This talk will discuss the surface chemistry of graphitic materials, with a focus on analysis by ultra-violet photoelectron spectroscopy (UPS). UPS and XPS measurements were collected from freshly cleaved HOPG in ultra-high vacuum and after exposures to ambient air. We observed an immediate surface contamination upon exfoliation in ambient air, followed by further growth and a dynamic composition change during increased exposure times. The advantages of UPS...
over XPS for the surface analysis of carbon substrates is highlighted and used for contamination characterization.

Sampling depths of UPS and XPS on graphitic materials

**LOCAL CHANGES TO THE STRUCTURE AND CHEMISTRY OF THICK MoS2 FLAKES DUE TO HEATING**

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Because of profound applications of MoS2 crystals in electronics, their oxidation is the subject of substantial interest. Particularly so, because pristine 2H-MoS2 crystals are n-type semiconductors, while Mo oxides might display p-type semiconducting behavior. Here, we report on oxidation of the surface of single MoS2 crystals, which were heated at a series of steps either by increasing heating time or by increasing temperature up to 500 °C. In the case of increasing heating time we observed triangular etch pits similarly to earlier MoS2 heating studies. However, while keeping the time constant and by increasing heating temperature a cross-over from a triangular etch pits to a completely different behavior has been observed. Using electron dispersion X-ray spectroscopy (EDS) at ambient conditions, we observed an increase of oxide content with increasing heating temperature and obtained an apparent activation energy for the oxidation process of the order of 1 kcal/mol. This value is at least 8 times smaller than an activation energy for surface formation of MoO3 and according to the literature points rather to physisorbed oxygen species. Our Auger electron spectroscopy (AES) results also pointed out toward the physisobred oxygen, similarly as our further heating studies within elevated relative humidity conditions. The Mo oxide leftovers after heating in the vicinity of 500 °C on the sample were investigated using atomic force microscopy (AFM) and showed dendritic structures. Surface appearance of those dendrites, their fractal
dimension between 1.61 and 1.66, and their surface distribution were reminiscent of the diffusion-limited aggregation (DLA) growth. On the basis of analysis of AFM topographs, we hypothesized that the DLA process was controlled by a surface diffusion of the initially physisorbed oxygen, which had to diffuse to reaction centers in order to facilitate the subsequent chemical conversion of MoS2 layers to volatile Mo oxides.

COLL 48

Copper-supported single layer MoS2 for higher alcohol synthesis from syngas: A DFT + kMC study

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Owing to its low cost, abundancy, and potential catalytic applications, molybdenum disulfide (MoS2) attracts a great deal of attention for rational designing of cheap and efficient catalyst for alcohol synthesis from syngas. Because of the inertness of basal plane, it is necessary to find way to activate MoS2 for enhancing its reactivity. Herein, by means of density functional theory calculations of reaction pathways and activation energy barriers, we show that MoS2 with sulfur vacancy row supported by the Cu(111) surface is a promising catalyst for higher alcohol synthesis from syngas. Our calculations suggest that the potential products of the synthesis include methanol, ethanol, formaldehyde, methane, and water, among which ethanol, methane, and water are thermodynamically favorable. The reactivity of the catalyst is traced to the strong MoS2-Cu(111) interaction which leads to enlargement of vacancy row region, and to the charge transfer from Cu to MoS2 resulting in a shift of the frontier states (d orbitals of the exposed Mo atoms) making it closer to the Fermi level. Kinetic Monte Carlo (kMC) simulations show that about 80% selectivity towards ethanol can be achieved with H2/CO ratio of 0.5-1.5 and at a pressure of 1-2MPa, an ideal condition for industrial catalysts. Overall, our results from DFT+kMC simulations provide insights into the reaction mechanism behind the conversion of syngas into the higher alcohols, and thus help providing guidelines for rational design of MoS2/Cu-based catalyst for higher alcohol synthesis from syngas.

COLL 49

Theoretical study on the conversion mechanism of methane on surface single atom catalysts

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With the increasing consumption of petroleum resources and the large-scale discovery of shale gas, natural gas hydrate and biogas, replacing oil by relatively abundant reserves of natural gas to produce liquid fuels and basic chemicals has become the
focus of research in academia and industry. However, the direct, nonoxidative routes suffer from a significant challenge of methane activation because CH\textsubscript{4} has low electron and proton affinity, zero dipole moment and high C-H bond energy of 439 kJ/mol. The single atom catalyst supported on the solid surface play a more and more important role in activating methane due to its high efficiency and stability in recent years. But the catalytic process is complicated and reaction mechanism is still not clear. We focus on the study of methane conversion mechanism on the solid surface by ab initio simulation, which may be helpful in designing high efficiency catalyst for industrial applications.

Yuan Liu

**COLL 50**

Key details of nerve-agent decomposition on single site Zr-based polyoxometalates revealed by a correlated multimodal approach

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Efficient protection of the population from chemical warfare agents (CWAs) is one of the most urgent and important tasks of science and technology. Recently, polyoxometalates have attracted attention as potential catalysts for nerve-agent decomposition. However, the improvement of their effectiveness requires an atomic-level understanding of CWAs decomposition. Here, we present our findings on the decomposition of a CWA simulant, dimethyl chlorophosphate (DMCP), by the zirconium polytungstate. Using a multimodal approach, combining synchrotron X-ray absorption and scattering with electron and vibrational spectroscopies and density functional theory calculations, we were able to probe dynamic changes of the structures of both the filtration materials and reactants, and identified the active site of the catalyst and the decomposition products. We showed that, on DMCP and Sarin exposure, the catalyst transforms from dimers to monomers with coordinatively unsaturated Zr(IV)-centers, which are a key intermediate in the nucleophilic hydrolysis catalytic mechanism. We found a strong similarity in
reactivity of DMCP and Sarin, and propose DMCP as a model system for future studies of CWA deactivation.

XPS spectra of Zr-POM exposed to GB and DMCP with fitted Gaussian components
Combination of data from multiple probes obtained during the prolonged exposure of ZrPOM to DMCP vapors reveals dissociation of Zr-POM dimers (D) to monomers (M), as shown schematically in the center.

**COLL 51**

Investing MOFs as a potential filtration media for the adsorption and decontamination of chemical warfare agents using *operando* synchrotron techniques

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Chemical warfare agents (CWAs) pose a threat to civilization worldwide and methods for their removal and decontamination are actively being sought. A decontaminating material must be able to capture and detoxify the released vapors. A predetermined understanding of the changes in the structural and electronic properties of filtration materials during exposure to CWAs still remains in its infant stages. The development of in-situ synchrotron research to study these properties will provide insight into the design and synthesis of filtration materials applicable for real world problems. Metal Organic Frameworks (MOFs) show promise as potential nerve agent decontamination catalysts. We recently found that zeolitic imidazolate based frameworks (ZIFs), a sub-class of MOFs, have shown to reactively adsorb sarin simulant, dimethyl chlorophosphate (DMCP). The changes observed in the X-ray absorption near edge fine structure (XANES) at the Zn center upon exposure to DMCP suggested the formation of new bonds. An increase in the amplitude of the pair correlations corresponding to the scattering contributions of Zn with DMCP during the reaction process is also observed using pair distribution function analysis (PDF). Insights into the mechanistic details sought out by using a multimodal approach investigated herein, reveal the necessary building blocks required to obtain a fundamental understanding of MOFs-CWA interaction necessary to validate the application of MOFs as filtration media.

COLL 52

Synthesis and assembly of dendrimer-nanocrystal hybrid superstructures

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The synthesis of size and shape-controlled nanocrystals (NCs) with a wide range of compositions now yield semiconducting, magnetic, metallic, and dielectric NCs that serve as ideal building blocks for the assembly of new mesoscale materials. These NCs can be thought of as "artificial atoms" who’s tunable electronic, optical, magnetic properties that are further enhanced/modified by the geometry of the NCs themselves and by the anisotropic coupling to neighboring NCs. We will briefly outline strategies to employ dendrons as surface ligands to direct the assembly of shape and size uniform NCs (single phase, core-shell (heterostructures), heterodimers, etc…). I will emphasize how tuning the relative size of the cores (spheres, roads, cubes, discs, octahedra, etc…) and the dendrimer capping shells can control the NC packing arrangement and number of nearest neighbors (valence/hybridization) and the strength of coupling (bonding) to nearby NCs in the resulting superlattices. We will explore the techniques (electron
tomography and x-ray scattering) need to three-dimensionally characterize the NC geometries and the spatial arrangement of the particles in thin films. Preliminary results on the spectral characterization of these dendrimer-NC hybrids will be presented. A combination of steady-state and ultrafast spectroscopy techniques will be employed. Specific attention will be focused on NC sizes and shapes that self-assemble like the “pieces of a puzzle” to allow access to new combinations of multifunctional materials. Concepts of supermolecular ligand design will be highlighted as a route to program the organization of NCs through interactions that are not exclusively dictated by the under NC’s geometry allowing an expanded design space.

COLL 53

Mechanism of nanocrystal self-assembly at an interface, followed by oriented attachment

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It has been reported that drop casting of a suspension of PbX (X=S, Se, Te) nanocrystals on an ethylene glycol liquid substrate results in the formation of atomically coherent 2-D sheets of a nanocrystal monolayer in thickness; these systems can be simple 2-D quantum wells, sheets with a square periodicity of voids, and sheets with a hexagonal periodicity of voids, resulting in a honeycomb semiconductor. It has been accepted that these two-dimensional systems point to a formation mechanism at an interface, probably the oil/air interface. However, there is much debate about which physical-chemical factors decide between simple quantum wells, and square and honeycomb superlattices.

I will present here our recent progress in this field which is based on in-situ GISAXS and GIWAXS measurements, and molecular dynamic simulations. For the square superlattice we could follow at the stages of the process, entailing (i) formation of a hexagonal layer of non-interacting particles at the oil/air interface, (ii) the desorption of ligands from the (100) facets enhancing the chemical/electrostatic interactions between these facets of adjacent nanocrystals, resulting in nanocrystal orientation and the gradual deformation of a hexagonal lattice into a square geometry, (iii) formation of a square ordered monolayer of nanocrystals, with all (100) NC axis upwards, (iv) formation of crystalline necks between the nanocrystals.

Second, we show what happens if the superlattice formation is made extremely slow, under a nearly saturated gas of the solvent: we observe silicene type honeycomb sheets with lateral dimensions in the 100 micrometer range. We also prepared silicene structures that extend in the vertical dimension over several unit cells. Finally, we studied the "atomic-like" and orientation defects in these systems.

COLL 54
N- and P-doped colloidal nanocrystal and nanowire assemblies

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Doping is used to control free carrier type and concentration in semiconductor materials. In bulk semiconductors, doping is conventionally achieved through impurity substitution, and less well-known, by controlling a material's stoichiometry. However, doping in low-dimensional, colloidal semiconductors presents both new opportunities and challenges. The electron and hole concentrations in colloidal nanocrystal (NC) and nanowire (NW) assemblies have often been manipulated by “remote doping,” exploiting the large surface-to-volume ratio of nanostructures to add atoms, ions, or ligands to the surface that serve as dopants. For example, we describe methods of 1) thermal evaporation and diffusion and 2) wet-chemical techniques to introduce extrinsic impurities to and non-stoichiometry through the nanostructure surface to passivate surface traps and dope NC and NW assemblies. However, the doping efficiency of colloidal nanostructures is often extremely low, such that only 1% of dopants yield carriers. These low doping efficiencies are consistent with increased ionization energies from quantum and dielectric confinement effects. We show for a given size nanostructure, where quantum confinement effects are fixed, the doping efficiency can be enhanced by >10-fold by encapsulating the NCs and NWs in high dielectric constant materials that reduce the dielectric mismatch between the nanostructure and its surroundings. We give examples where n- and p-type semiconductor NC and NW assemblies are used to construct flexible, electronic transistors and integrated circuits and optoelectronic solar photovoltaics and photodetectors.

COLL 55

Synthesis and plasmonic properties of colloidal metal oxide nanocubes

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The past decade has brought rapid progress on chemical strategies to introduce dopant impurities into colloidal nanocrystals as they grow. In several cases, the shape of the resulting nanocrystals has differed from their undoped analogues, raising questions about possible mechanisms for dopant-induced shape effects. For the case of F doping in In$_2$O$_3$ nanocrystals (F:In$_2$O$_3$), we delineate a dual role of F as a dopant and shape-directing agent. Two primary environments for F dopants are detected using $^{19}$F solid state NMR, one of which is associated with the NC surface based on $^1$H-$^{19}$F correlation spectroscopy. We hypothesized that the surface F preferentially stabilizes the (100) crystalline facets leading to the cube morphology, which is supported by surface defect formation energies calculated using DFT. The great majority of the F, however, acts as an aliovalent substitutional dopant anion. The resulting high concentration of free electrons renders the nanocrystals plasmonic, with infrared frequency resonance modes. Distinct spatial modes of localized surface plasmon resonance are apparent in
FTIR spectra of nanocrystal ensembles and are directly visualized by electron energy loss spectroscopy mapping in a scanning transmission electron microscope.

**COLL 56**

**In situ observation of nanocrystal chemistry**

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Although colloidal nanocrystals of many different materials can be synthesized in high quality in respect of size, shape and crystallinity, our understanding of their formation and the involved chemical reactions is still rather poor. We will present detailed studies on nucleation and growth as well as ion exchange processes in nanocrystals. These include mass spectrometric, optical, electron microscopic and x-ray synchrotron experiments.

**COLL 57**

**Synthesis and properties of imperfect nanomaterials**

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Recently, the lattice strain and cation vacancies were shown to have a tremendous impact on the properties of materials. For instance, strain can modify the chemisorption properties of the metal considerably and hence can dramatically affect the catalytic performance of materials. In turn, amorphous materials or materials enriched with vacancies also revealed promising properties as electrocatalysts and cathode materials for Li⁺-ion, Na⁺-ion, etc batteries. We will present the synthetic approaches toward synthesis of imperfect nanomaterials. We will show how the in-situ studies on the mechanism of nucleation and growth of nanoparticles can facilitate the design of highly strained core/shell heterostructures and multicomponent nanoparticles with high concentration of vacancies for catalytic and electrocatalytic applications. We will discuss the structural stability of imperfect nanostructures.

**COLL 58**

**Stoichiometric preparations of iron oleate to improve the reproducibility of iron oxide nanoparticle syntheses**

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Iron Oleate has long been one of the most popular precursors for the synthesis of iron oxide nanoparticles. This is true despite the fact that it is not commercially available and must be custom synthesized. There are a handful of related syntheses that are in common use, but reproducibility of the synthesis is a significant concern. Iron oleate does not readily form a simple complex with one iron atom bonded to three oleate ligands as one might imagine. Instead, iron oleate often exists as a complex mixture of species that includes a series of oligomeric species with iron atoms bonded to each other through oxo bridges as well as other structure. This non-stoichiometric mixture is not easily purified as iron oleate resists the most common purification approaches. Iron oleate can not be recrystallized, as it does not crystallize and instead forms an oil or glass depending upon its temperature. Washing approaches are difficult to reproduce as the oleate ligands can be very labile, and repeated washes will continue to remove oleate ligands until it finally forms an insoluble solid. This lability of the oleates also make it difficult to purify the compound through chromatography as the compound can decompose on the column. Unfortunately, differences in the precursor synthesis can lead to difficulty in reproducing nanoparticles syntheses. We will discuss two approaches that have been demonstrated to yield highly reproducible iron oleate precursors. In the first approach, we produce iron oleate through the decomposition of another organometallic species in an excess of oleic acid yielding a solution of known stoichiometry that can be used without purification. In the second approach, judicious selection of reagents, solvents, and reaction conditions can yield an isolated compound of pure iron oleate with an iron:oleate ratio of exactly 1:3. These compounds can then be used to enhance the reproducibility of iron oxide nanoparticle syntheses. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States government.

COLL 59

Molecular simulations of separations of enantiomer using chiral stationary phases

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Chromatographic separation is a dynamic process, with the interactions between the drug and the chiral stationary phase mediated by the solvent. We use explicit-solvent fully atomistic molecular dynamics (MD) simulations, permitting all the interactions between the atoms constituting the polymeric chiral stationary phase (CSP), the solvent molecules and the drug molecule, to better understand the chiral recognition mechanism that makes the separation possible. Using amylose tris(3,5-dimethylphenyl carbamate) (ADMPC) as our prototype, three different solvent systems, and ten different racemates as solutes, we seek to find a molecular dynamics average quantity that could serve as a metric that predicts which of the two enantiomers will elute first.
and also correlates with the ratio of retention times for enantiomers. The ADMPC polymer provides to the approaching enantiomer a dynamic structural landscape that differs from solvent to solvent. Several MD average quantities related to hydrogen-bonding lifetimes correlate with the ratio of retention times for the enantiomers. One of these quantities provides a prediction of the correct elution order 90% of the time, and the ratios of these quantities for the enantiomers provides a correlation (0.85 coefficient) with the experimental separation factor (the ratio of retention times).

We have used both emi-rigid models for the ADMPC and fully flexible models. We have compared the results from the two models and found that improved prediction are obtained with a restricted model. Using periodic boundary conditions, we also simulated “infinite” length polymer chains to model a more macroscopic view.

**COLL 60**

**Dynamics of phospholipid membranes beyond thermal undulations**

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Understanding the morphology and molecular dynamics of phospholipids is very challenging, because of multiple length- and time-scales involved. Our contribution concentrates on the molecular motion in the time range of a few picoseconds to ~ 150 ns, studied by neutron spin echo (NSE) spectroscopy. This range is typically theoretically modelled by using a model developed by Zilman and Granek (ZG). We demonstrate that a more detailed analysis reveals that ZG describes the data only in an intermediate time region, whereas the region of fast motion is dominated by the molecular motion of the fatty acid tails, while the slow diffusion also affects the time region of NSE. A better understanding of the NSE result will be beneficial for the overall understanding of liposomes. The comparison of NSE data of numerous phospholipids confirms its universal behavior.

**COLL 61**

**Peptoid structure impacts adsorption of water-soluble peptoids to lipid bilayers**

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Small organic molecules may adsorb to and perturb the physical structure of lipids in the mammalian plasma membrane, causing changes to the conformation and function of transmembrane proteins. These non-specific interactions can also impact
bioaccumulation and toxicity. We used the label-free nonlinear optical method second harmonic generation (SHG) to monitor adsorption of therapeutically-relevant concentrations of water-soluble N-substituted glycine oligomers (peptoids) to artificial lipid membranes. Peptoids have exhibited enhanced biostability compared to proteins and peptides, and have shown promise as therapeutics and as nanomaterials. To advance peptoid-based technologies, systematic studies of structure-property relationships are needed to predict their behavior in physiological conditions. Our studies quantified the binding affinities of peptoids (with varied 3D structures and individual substituent features) to phospholipid membranes of varying phase, cholesterol content, and head group charge.

**COLL 62**

**Lipid motion reflects additive-induced effects on the dynamic and phase state of phospholipid membranes**

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Microscopic dynamics of plasma membrane is a prime influencer of various cellular processes, such as cell signaling, membrane trafficking, permeability, cell division, fusion, etc. Studies of model phospholipid membranes are instrumental in probing the influence of membrane additives on the microscopic dynamics, and, thus, properties of the membrane. Quasielastic neutron scattering (QENS) is a highly suitable technique for investigating microscopic dynamics of lipids in membranes. It provides both spatial and temporal information and is sensitive to the dynamics on pico- to nanosecond time scale and Angstrom- to nanometer length scale. Both the localized and long-range translational (linked to lateral diffusivity) lipid motion components can be probed simultaneously. Temperature dependence of the elastic scattering intensity is used to investigate phase behavior of the membrane associated with the microscopic dynamics of the lipids. Lipid motion undergoes qualitative changes upon a phase transition (such as gel to fluid) in the membrane. Besides, quantitative dynamic changes, such as increase or decrease in the lipid lateral diffusivity in the given phase state, are often observed upon incorporation of an additive in the membrane. We review our studies of phospholipid membranes with various additives, from cholesterol to anti-inflammatory drugs to antioxidants to antimicrobial peptides. The effects on the dynamic and phase state of the membrane vary greatly, depending on the location of the additive within the membrane and the strength of its interaction with the lipids, composition of the membrane, and so on. In some cases, the membrane phase transition is eliminated altogether, even though the additive’s concentration is too low to induce measurable structural changes in the membrane. Finally, we discuss possible expansion of systems amenable to studies of microscopic lipid dynamics.

**COLL 63**
Vascular smooth muscle cells: Key players in arterial aging

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Vascular smooth muscle (VSM) cells play an integral role in regulating matrix deposition and vessel wall contractility via interaction between the actomyosin contractile unit and adhesion structures formed at the cell membrane that mechanically link the cell to the extracellular matrix. This study aims to investigate age-induced structural changes in VSM cells that result in their impaired ability to develop contractile function. VSM cells were isolated from soleus feed arteries from young (4 months) and old (24 months) male Fischer 344 rats. Quantitative analysis of fluorescence images showed a significant reduction in essential proteins required for cellular contractility and adhesion in old cells by comparison with young ones. In addition, atomic force microscopy measurements showed an increase in cell stiffness and integrin-mediated adhesion to the matrix in old VSM cells. Moreover, upregulation of ROCK activity in old cells was not able to rescue the reduced contractile state in aging. Taken together, the results of this study suggest that age-induced changes at the molecular level in VSM cells play a central role in the reduced arterial contractile function in aging.

COLL 64

Liposome delivery and release driven by molecular recognition

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Liposomes are effective medicinal nanocarriers due to their ability to encapsulate and deliver a range of therapeutic cargo. While liposome formulations have been approved for clinical use, delivery properties would be improved by enhancing control over the release of contents as well as diseased-cell selective delivery. Toward this end, research has focused on using either pathophysiological conditions (passive release such as pH, redox or enzyme overexpression) or external stimuli (active release such as light, heat and ultrasound) to control release. We have been seeking to expand this toolbox by exploiting molecular recognition events to trigger liposome delivery and content release based on the chemical makeup of diseased cells. We will describe designer liposomes containing synthetic lipid switches that undergo conformational changes that trigger release of liposomal contents upon the binding of target molecules. This will include the design and synthesis of lipid switches, liposome release assays,
analysis of changes in liposome properties upon target binding, and cellular delivery studies. This work provides promising strategies for enhancing the ability to control liposome targeting and release in drug delivery applications.

COLL 65

Solute partitioning and solvation in lipid membranes: Microscopic origins of bioaccumulation

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Time-resolved fluorescence and differential scanning calorimetry were used to determine the partitioning of coumarin 152 (C152) into large unilamellar vesicles composed of binary mixtures of two phosphatidylcholines (12:0/12:0 DLPC and 14:0/14:0 DMPC) and vesicles composed of binary mixtures of a phosphatidylcholine and a phosphatidylethanolamine (14:0/14:0 DMPC and 14:0/14:0 DMPE). Time-resolved fluorescence indicated that C152 partitioning into DLPC/DMPC mixtures showed nearly ideal behavior that was described with weighted contributions from C152 partitioning into pure DLPC and pure DMPC vesicles. In contrast, C152 partitioning into DMPC/DMPE mixtures was distinctly non-ideal. For DMPC/DMPE lipid vesicles having DMPC mole fractions between 10-80%, C152 partitioning into the bilayer was measurably enhanced near the melting temperature, relative to expectations based simply on weighted contributions from C152 partitioning into vesicles comprised of pure lipids. For vesicles comprised of pure DMPE, C152 shows almost no partitioning into the membrane with ≥80% of the solute remaining in the buffer solution at temperatures between 10-50 C. These findings will be presented in the context of solute accumulation in biological membranes and its impact on solute persistence in environmental systems.

COLL 66

Dynamic interplay between PA and DGPP regulates lipid negative charge and protein-lipid interactions

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Diacylglycerol pyrophosphate (DGPP), a phosphorylated form of phosphatidic acid (PA), is an uncommon membrane lipid found in plants, yeast, and other microorganisms but never in mammals. DGPP is formed from PA, which, in plants, is formed as a response to stressful environmental conditions such as extreme temperature, salinity, and pathogen attack. The function of the formation of DGPP during stress is unclear; however, DGPP is unique as it is one of few membrane lipids with a pyrophosphate in the head group. This pyrophosphate head group is likely crucial to the function of DGPP. Furthermore, genetic approaches have thus far failed to elucidate a function for DGPP, other than verify its involvement in stress signaling. Therefore, the physical-
chemical and protein-lipid interaction properties were analyzed to elucidate the function of DGPP. We focus on the ionization of the pyrophosphate head group in model membrane systems of increasing complexity. Specifically, we evaluate the ionization of DGPP when present together with PA in model systems of phosphatidylcholine or phosphatidylcholine plus phosphatidylethanolamine. Additionally we evaluate the binding of PA binding proteins to DGPP. The results shed light on the function of the enigmatic stress signaling lipid DGPP.

**COLL 67**

**From lipid vesicles to lipid onions: A molecular-dynamics simulation study**

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We present coarse-grained molecular dynamics simulation results of three-component lipid vesicles in contact with a fourth component, which is a small molecule. The lipid components of the vesicle consist of cylindrical A, B and C lipids; where C is strongly interacting with B, C is weakly interacting with A and itself, while the interactions between A and B are neutral. Rigid domains consisting of B and C lipids emerge as the concentration of C lipids is increased in the vesicle. Further increase in size of these domains is seen as the concentration of B and C is increased relative to A and results in instability of the vesicle where the domains evolves into buds and break away from the vesicle. This can be likened to a two-component lipid system composed of rigid domains in a fluid matrix, where an increase in domain size relative to the radius of the vesicle leads to instability. These domains are in-register and are relatively symmetric in both inner and outer leaflets of the vesicle. However, in the presence of a small molecule, this symmetry is broken and depending on the affinity and concentration of the small molecule, the vesicle transitions into an onion-like configuration (vesicle within a vesicle), where the small molecule resides between the two bilayers and reestablishes the symmetry of the domains. These phenomena can be understood as phase separation dynamics on the surface of a sphere. We plan to verify the simulation results through optical and fluorescent microscopy observations and through Landau-Ginzburg-type field theoretic descriptions of both the lipid composition and the effects of the small molecule additions.
Porous shells on gold nanorods

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Gold nanorods exhibit tunable plasmon resonances that vary over the visible and near-infrared wavelengths of the electromagnetic spectrum. The application space for these nanomaterials includes optical sensing, chemical imaging, and photothermal molecular release. Controlling the surface chemistry of the rods is required to enable these applications. In this talk I will present recent work on controlled growth of mesoporous silica and porous metal-organic-framework (MOF) shells on gold nanorods, in ways that maintain the porosity of the nanoscale shells.
Impact of surface chemistry in multimetallic nanoparticle synthesis and performance

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Metal-ligand chemistry impacts nearly every aspect of nanoparticle formation, physical properties, and utility. We develop methods to study and leverage these interactions to produce highly tailored multimetallic nanoparticles with dimensions spanning the nanoscale (1-100 nm). Here, we discuss how metal-ligand interactions may be used to mediate the incorporation and distribution of metals in and on discrete, colloidal nanoparticle substrates, as well as their optoelectronic properties once formed. In particular, we demonstrate that nanoparticle ligand chemistry may be used to access previously unobserved mixtures of metals such as continuously tunable Au-Co composition ratios, unique distributions of metals at the surface of a colloidal particle, as well as composition-tunable optoelectronic features. Underpinning these studies are the development of analytical techniques to quantitatively track and ultimately tune the surface chemistry of these nanoparticles in order to create translational insights into the role of nanoparticle surface chemistry in their performance downstream. Together, these results provide mechanistic platforms for the development of nanoscale alloys and other bimetallic structures that we demonstrate are promising for a wide variety of applications ranging from light-driven catalysis to multimodal bioimaging.

Deconstructing nanoconstructs

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This talk will discuss whether ligands can be separated from their particle scaffolds when evaluating and describing nanoconstruct function. We will describe how non-traditional analytical tools can be used to provide insight into nanoparticle growth and ligand distribution on different shapes of gold nanoparticles.

Crystal growth and surface chemistry of metal halide perovskite nanomaterials

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The remarkable solar performance of lead halide perovskites can be attributed to their excellent physical properties that present many mysteries, challenges, as well as
opportunities. Better control over the crystal growth of these fascinating materials and better understanding of their complex solid state chemistry would further enhance their applications. Here I will first report new insights on the crystal growth of perovskite materials and the solution growth of single crystal nanowires and nanoplates of methylammonium (MA), formamidinium (FA), and all-inorganic cesium (Cs) lead halides perovskites (APbX$_3$) via a dissolution-recrystallization pathway. The surface chemistry of these soft ionic crystal materials is quite different typical semiconductors and their impact to physical properties was studied using such well defined high surface area nanostructures. Moreover, chemical strategies to stabilize the metastable perovskite phases, such as FAPbI$_3$ and CsPbI$_3$, have been developed by using surface ligands to manipulate the delicate thermodynamic and kinetic balance between 3D and 2D layered perovskites. We further demonstrated high performance room temperature lasing with broad tunability of emission with these single-crystal perovskite nanowires. The excellent properties of these single-crystal perovskite nanostructures of diverse families of perovskite materials with different cations, anions, and dimensionality make them ideal for fundamental physical studies of carrier transport and decay mechanisms, and for enabling high performance semiconductor lasers, LEDs, and other optoelectronic applications.

**COLL 72**

**Surface versus solution chemistry: Manipulating nanoparticle shape and composition through metal-thiolate interactions**

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Nanostructures with well-defined crystallite sizes, shapes, and compositions are finding use in a diversity of applications. Seeded growth is a promising strategy to achieve shape-controlled nanostructures, where specific structural features can be directed by the underlying seed symmetry. This presentation will discuss the use of thiophenol derivatives during the seed-mediated synthesis of Au-Pd nanostructures. As we found, these thiophenol derivatives are capable of different metal-thiolate interactions, both at the surface of the growing nanocrystals and in solution with the metal precursors. Specifically, our systematic analysis revealed that the symmetry and composition of the bimetallic nanoparticles can be tuned as a function of additive binding strength and concentration, with symmetry reduction observed in some cases. Furthermore, additives with both thiol and amine functionalities facilitate random branching on the octahedral seed. Significantly, this work highlights how the dual roles of synthesis components can be exploited to achieve high quality bimetallic nanostructures.

**COLL 73**

**Leaching of metal nanostructures through oxidative etching and its influence on the catalytic reduction of 4-nitrophenol**
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The fundamental understanding of liquid-phase catalytic reactions is unavoidably complicated when the catalyst is prone to leaching since questions inevitably arise as to the true nature of the catalyst. While the catalytic reduction of 4-nitrophenol by borohydride is widely accepted as a trusted model reaction, it has faced little scrutiny concerning the potential impact of leached species or the appropriateness of assigning catalytic activity to the inserted nanostructures without rigorous experimental verification. Here, we present results from a spectroscopically monitored split test in which supported silver catalysts are physically separated from the reactants midway through the reaction. It is unambiguously demonstrated that the influence of leaching is far from benign, instead acting to extinguish the catalytic activity of the inserted nanostructures while giving rise to an unsupported species that is the true catalytic entity. With only sub-monolayer quantities of silver leached from the supported structures, the unsupported species must be exceedingly catalytic. Moreover, it is shown that leaching is inherent to aqueous media containing dissolved oxygen, without which the supported nanostructures remain catalytically active. With the same nanomaterial being able to act as either a heterogeneous catalyst or as a reservoir from which leached metal is derived, such influences have undoubtedly compromised prior studies. We, nevertheless, capitalize on the sensitivity of 4-nitrophenol reduction to leached species by using it as a reaction-based indicator able to quantitatively determine the time-dependence of the leaching process and enhancements to oxidative etching when silver, copper, palladium, platinum, and gold are exposed to chloride ions.

COLL 74

Surface chemistry of colloidal lead halide perovskite nanocrystals

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Colloidal lead halide perovskite nanocrystals (NCs) are intensely pursued as highly promising, low-cost light-emitting materials with wide color gamut. These NCs exhibit unprecedented luminescent properties – narrow-band emission with high quantum efficiency, covering the whole visible spectral range and extending into near-infrared, all obtained without epitaxial overcoating of the NC surfaces for electronic passivation [1]. Their processing and luminescent properties are challenged by the lability of their surfaces. Surface and sub-surface atoms are likely directly involved in all possible chemistry equilibria and transformations. The processing and optoelectronic applications of perovskite NCs are hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface capping molecules during isolation and purification. To address this issue, we developed a new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules [2].
particular, this class of ligands allows for the isolation of clean NCs with high photoluminescence quantum yields of above 90% after four rounds of precipitation/redispersion. On the example of CsPbBr$_3$ NCs, we rationalize the typical observation of a degraded luminescence upon aging or the luminescence recovery upon post-synthesis surface treatments using a simple surface-structure model, supported by DFT calculations [3]. Healing of the surface trap states requires restoration of all damaged PbX$_6$ octahedra and establishing a stable outer ligand shell. Restoration of such a structure was attained using a facile post-synthetic treatment with a PbBr$_2$+DDAB (didodecyldimethylammonium bromide) mixture. In practical terms, we demonstrate that such an approach is useful to obtain purified CsPbBr$_3$ NCs samples, washed up to three times in several solvents, with near unity photoluminescence quantum yields and long-term colloidal stability.

COLL 75

**Characterizing the organic coating of quantum dots using NMR spectroscopy**

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Colloidal nanocrystals offer flexible nanoscale platforms with unique optical and physical properties. Furthermore, such properties can be tuned by varying the nature and overall structure of the surface coating. Despite the remarkable advances in the growth and functionalization of these materials, information about the molecular arrangements of those ligands remains limited. We hereby apply several NMR spectroscopy techniques to characterize the ligand arrangements of both, as prepared hydrophobic colloidal nanocrystals and after phase transfer to water. We first combine the proton signatures of the ligands with diffusion ordered spectroscopy (DOSY) to distinguish surface-coordinated ligands from those freely-diffusing in the medium. We then combine $^1$H, $^{31}$P and HSQC spectroscopy techniques to identify the composition of the surface bound ligands. Finally, from comparison between the sharp signature(s) of specific groups in the surface-bound ligands to external standards we were able to extract estimates for the average number and stoichiometry of ligand compositions per nanocrystal.

COLL 76

**Dynamic ligand exchange and surface charge density modulate the optical properties of CdSe quantum dots in water as a function of pH**

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Solution pH and ligand lability modify the optical bandgap of CdSe quantum dots (QDs) in water due to the ability of water to act as a non-inert solvent at the QD surface. Water-soluble QDs are desirable for photocatalytic and biosensing applications, and are commonly prepared through capping with strong-binding thiolate ligands such as 3-mercaptopropionic acid and dihydrolipoic acid. Thiolate capping ligands, however, i) scavenge holes from photoexcited QDs and thereby competitively inhibit hole transfer to reactants during photocatalysis, and ii) form disulfide bonds upon oxidation and dissociate from the QD surface, leaving the inorganic core exposed to the solution environment. To avoid the use of thiolate capping ligands, we use either a phosphonoalkanoic acid or HCl to strip the QD of its native oleate ligands and effect a phase transfer from hexanes into basic water, resulting in effectively “ligand-less” QDs. We use a combination of ground state optical spectroscopies, nuclear magnetic resonance spectroscopy, and x-ray photoelectron spectroscopy to characterize the interaction of hydroxide ions with the QD surface as a function of pH. As the pH of the solution increases, the optical bandgap of these “ligand-less” QDs shifts to lower energy, which we attribute to an increase in negative charge density at the QD surface as the pH increases through both covalent and electrostatic interactions of hydroxide ions with the QD surface.

Gold nanoparticle-blood serum interaction assay reveals humoral immunity development and immune status of animals from neonates to adults

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The interaction between gold nanoparticles (AuNPs) and blood plasma or serum proteins has been well studied by many research groups. Upon mixing AuNPs with a blood plasma or serum samples, a protein corona is formed almost instantly on the AuNP surface. In our previous research, we demonstrated that the size and the composition of this protein corona is dependent on the disease status of the blood donor. Here, we report our most recent finding that links the protein corona composition of the AuNP to the immunity and immune status of murine and bovine models from
neonates to adults. The average particle size of the gold nanoparticle-serum mixture, measured by dynamic light scattering, corresponds positively to the immune status and activity of the subject. A well-developed, functional immune system is paramount to combat harmful attack from pathogenic organisms and prevent infectious diseases. Our study established the feasibility of a convenient test not only for monitoring the immune function development from animals and humans, but also for detecting active immune responses during infection.

COLL 78

Affinity of neutral Lewis bases and ion pairs for colloidal nanocrystal surfaces

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Using 1H and 31P nuclear magnetic resonance spectroscopy, we have probed the steric and electronic factors that determine the binding affinities of ligands to CdSe surfaces. We have evaluated the binding affinities of neutral ligands relative to tri-n-butyolphosphine and shown that the packing density is strongly impacted by the ligands steric bulk. I will also discuss the binding of anionic ligands that balance charge with outer sphere cations to stoichiometric nanocrystals. The tight binding of carboxylate, phosphonate, and carbamate anions makes the preparation and isolation of stoichiometric nanocrystals with neutral donor ligands especially challenging. Moreover, our studies have shown that the stabilization of colloidal dispersions by neutral ligands is poor, suggesting that nanocrystals are rarely stabilized by this coordination motif alone.

COLL 79

Optoelectronic impacts of surface chemistry in small noble metal nanoparticles

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Small gold nanoparticles (AuNPs, ~1.4–2.2 nm core diameters) exist at an exciting interface between molecular and metallic electronic structures. These particles have the potential to elucidate fundamental physical principles driving nanoscale phenomena and to be useful in critical applications ranging from catalysis to bioimaging. Here, we consider the role of particle surface architecture and composition on the electronic structure of the materials, and ultimately how the resulting optoelectronic features may be used in downstream energy transfer applications. Specifically, we demonstrate the surface chemistry-dependent photoluminescent properties of aqueous, phosphine-terminated AuNPs) as a function of ligand shell identity. No emission is observed from these particles when passivated with phosphine-based ligands, however the introduction of sulfur-containing ligands initiates photoluminescence, with quantum
yields approaching 4%. With correlation between surface chemistry and AuNP emission properties in hand, we study the use of these photoluminescent events in energy transfer applications. In these experiments, we use NIR-emitting AuNPs to excite ytterbium(III) emission and describe both the efficiency and mechanism of the energy transfer process. These results lay a foundation for the incorporation of emissive AuNPs in a variety of applications that require controlled energy transfer such as catalysis, sensing, and energy harvesting technologies.

COLL 80

Enhancing humoral immunity to subunit vaccines through engineered immunogen binding to aluminum hydroxide adjuvant

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The kinetics of antigen availability following immunization impact follicular helper T cell priming, germinal center responses, and ultimate antibody production, but clinically-relevant methods to control the duration of antigen delivery to lymph nodes in subunit vaccines are lacking. We conjugated antigens derived from the gp140 HIV envelope trimer with a phosphoserine (pSer) peptide that binds tightly to the most common clinical adjuvant, aluminum hydroxide (Alhydrogel, or alum). Site specific modification of an engineered outer domain (eOD) gp120 or stabilized SOSIP trimer immunogen with varying numbers of pSer groups allowed the binding strength to alum to be tuned and alum-bound antigens were presented from alum particle surfaces with a defined orientation. pSer-antigen conjugates in alum could be tuned to steadily release antigen from an injection site over multiple weeks in mice. This persistence led to improved lymph node uptake and colocalization of antigen with B cell follicles. Ultimately, a 20-fold increase in titer relative to the unmodified protein was observed four weeks after primary immunization with both pSer-eOD and pSer-SOSIP conjugates, and long-lived plasma cells in bone marrow were doubled by immunization with pSer-modified immunogens. Additionally, conjugation of pSer linkers to the base of SOSIP trimers minimized the formation of base-specific antibodies, suggesting that antigen arrives in lymph nodes still bound to alum particles. Overall, pSer-antigen conjugates elicited significant increases in antibody titers and altered specificity of the humoral response through controlling the display of antigen on the surface of alum.

COLL 81

Engineered materials as tools to study immune function

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Lymph nodes are key tissues that coordinate immune function. In this talk I will present some of the new ways we are studying the interactions of engineered materials with immune tissues to inform design of vaccines and immunotherapies. For example, we are working to understand how the local concentrations of drugs in lymph nodes impacts the development of immune cells expanding and differentiation in these sites. Our data reveal that different types of T cell responses – effector, memory, regulatory – can be produced against the same antigen by locally altering metabolism in lymph nodes during T cell expansion. We are applying this idea to generate T cell subsets specialized to combat tumors during cancer vaccination. As another example, we are using quantum dots as tools to control how the combinations, densities, and concentrations of self-antigens displayed in lymph nodes control the development of immune tolerance. Understanding these design parameters could inform design of new therapies for autoimmune diseases such as multiple sclerosis and type 1 diabetes. Lastly, recent studies reveal many biomaterials exhibit intrinsic features that activate, suppress, or modulate immunity, even in the absence of other immune signals. I will discuss our work to characterize how these immunological interactions change as common polymeric vaccine carriers degrade in immune cells and in lymph nodes. Understanding how the immunological profile of biomaterials evolves during delivery could enable materials that help actively direct immune response through their intrinsic immunogenic features. Conversely, these intrinsic immunogenic features create some challenges for rationale design, since the carrier can alter the response to other vaccine or immunotherapy components. Motivated by this idea, I will present our work to leverage self-assembly of immune signals to build nanostructured materials that mimic attractive features of biomaterials, but that are assembled entirely from immune signals.

COLL 82

Nanoparticle immunotherapy: Towards a cancer-curative vaccine

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The ability to trigger a patient’s immune response against cancer is an appealing therapeutic alternative to the existing use of radiation and chemotherapy. While our bodies normally safeguard us against cancer through immune surveillance, immunosuppressive changes in the tumor microenvironment impair normal immune functions. Boosting the immune response in the presence of appropriate cancer antigens is one approach to reactivating normal immune defense mechanisms. Nanoparticle platforms present a means to co-deliver cancer antigens and immune stimulants. We have engineered an immunogenic nanoparticle that is capable of efficiently housing multiple components in a biocompatible mesoporous silica nanoparticle core coated by a lipid shell. The shell incorporates pathogen-associated molecular patterns (PAMPs) such as the bacterial lipopolysaccharide (LPS)-derived
monophosphoryl lipid-A (MPL-A) as an adjuvant that activates Toll-Like Receptor (TLR)-4 on antigen-presenting cells (APCs). The mesoporous core is designed to house tumor neoantigens, and here we demonstrate proof-of-principle using the model antigen ovalbumin. Our research shows specific uptake of our immunogenic nanoparticles by immune cells, with low or no uptake by stromal cells. Additionally, an unprecedented synergistic effect resulted from sequential presentation of antigen and adjuvant highlighted by elevated antigen presentation and enhanced APC activation. In summary, our presentation will highlight the ability of “nanoparticle immunotherapy” to stimulate effective antigen-specific immune responses.

COLL 83

Macrophage-mediated delivery of bioorthogonal nanozymes for targeted cancer therapy

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Targeting the tumor microenvironment has emerged as a prominent strategy in cancer therapy to overcome the lack of specificity of conventional chemotherapy techniques. Macrophages have been shown to migrate across chemoattractant gradients and are actively recruited to tumor regions. This characteristic makes macrophages particularly attractive as a delivery vehicle to access solid tumors, which is normally difficult to reach by conventional targeting strategies. This immune cell-based delivery strategy has prolonged circulation time and excellent biocompatibility. We have created a strategy to engineer macrophages with the catalytic ability to activate prodrugs, that can trigger unlimited payload release with controlled kinetics and excellent targeting efficacy. In our study, we engineered macrophages as a delivery vehicle for gold nanoparticles (AuNPs) encapsulated with transition metal catalysts (TMCs). These catalyst embedded nanoparticles (Nanozymes) can activate a prodrug by a bioorthogonal cleavage reaction in the cellular environment, as reported in our previous studies. By virtue of selective bioorthogonal chemical activation, we facilitated controlled release of drug molecules selectively at the targeted site reducing the systemic toxicity of the therapy. We tested the efficacy of engineered macrophages in a coculture model with cancer cells. Significant cell toxicity was achieved even at the lowest concentration of the prodrug administered. Our strategy here combines targeting ability of cell-based drug delivery with bio-orthogonal activation of chemotherapeutic prodrug, providing an approach for next generation drug delivery systems.

COLL 84

Long term delivery of antibodies from hydrogels for local cancer immunotherapy
Antibodies for immunotherapies have shown great promise in the treatment of cancer but efficacy is often limited by tumor uptake after intravenous injections. To improve efficacy, we are developing injectable hydrogels for the local sustained delivery of antibody conjugates (~100 days from a single injection) to enhance current and future immunotherapies. Sustained infusion will yield a tumor antibody steady-state concentration ($C_{ss}$) above the for extended periods. Recently, we developed a three-component drug delivery system for competitive affinity release of streptavidin-antibody conjugates from agarose-desthiobiotin hydrogels via controlled dissolution of sparingly soluble biotin derivative pellets. The streptavidin-antibody is localized in the gel through desthiobiotin complexation, and dissolution of the biotin derivative displaces desthiobiotin from the streptavidin-antibody conjugate. Streptavidin release was tuned by altering oleyl-biotin concentration to achieve first-order release for 150 days. First-order release of streptavidin-Avastin was tuned for over 100 days by varying the dissolution rate of oleyl-biotin, which was controlled the total oleyl-biotin concentration. The bioactivity and stability of streptavidin-Avastin was confirmed by HUVEC tubulogenesis assays and LSPR binding studies. The system was determined to be non-cytotoxic through cell viability assays. For long term release applications, we require a hydrogel that does not elicit a foreign body response to prevent formation of a surrounding fibrous capsule. Therefore, we developed an injectable hydrogel composed of poly(carboxybetaine) co-polymers that crosslink through biorthogonal strain-promoted alkyne-azide cycloaddition. The hydrogels are both low-fouling and low-swelling, and suitable for long term antibody delivery.

**COLL 85**

**Electrical “suturing” of polyelectrolyte hydrogels to reseal cut or damaged tissues**

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This talk will present studies from our lab on the electrically induced adhesion of hydrogels and beads made from polyelectrolytes. The basic phenomenon involves crosslinked acrylate hydrogels made with either anionic co-monomers (such as sodium acrylate) or cationic co-monomers (such as aminated acrylates). When a rectangular strip of a cationic gel (connected to an anode) is contacted for just a few seconds with a strip of anionic gel (connected to a cathode) under a voltage of ~ 10 V, the two gel strips form a strong adhesive bond. When the polarity of the electrodes is reversed, the phenomenon is reversed, i.e., the gels can be easily detached.

While the above phenomenon of ‘electro-adhesion’ has been reported before for hydrogels, we show that it is much more general and widespread. Specifically, we can
substitute either of the above gels with a spherical bead made using charged biopolymers such as chitosan or alginate. The same electro-adhesion works to join beads to gels, or two beads to each other. In turn, electro-adhesion can be applied for the pick-up and drop-off of soft cargo, and for the sorting of beads. Most interestingly, the same phenomenon also works with certain human tissues. That is, many tissues are anionic, and we show that cationic gels can be electro-adhered to them. We thereby demonstrate that cuts or tears in tissues can be electro-sealed using beads or gel strips. As an extreme case, two severed pieces of a tube can be stuck back together using a gel strip that spans both cut segments; this is thereby an example of a needleless suture using only hydrogels and an electric field.

**COLL 86**

**Thermo-reversible bioadhesives based on cohesive failure**

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Reversible bioadhesive has emerged as an advanced wound closure method in recent years. A ‘on’ state makes the adhesive easy to apply and show immediate effect of adhesion to injured tissue, and a ‘off’ state is triggered after the patient is safely transferred to hospital, or painless removal is demanded after the wound is completely healed. Both physical and chemical approaches have been studied by using bioinspired microarray or reversible covalent bonding at the interface.

Here we will discuss a new reversible bioadhesive design based on cohesive failure. The key to our reversible bioadhesive is the use of a thermo-responsive polymer gel (TPG) combined with a seed layer that promotes strong adhesion between the TPG and tissue via non-covalent interactions, including hydrogen bonding, electrostatic interactions and hydrophobic interactions. This approach uses a FDA approved food additive as the seed layer, which is proved to be biocompatible and biodegradable. Thermo-responsive polymers, such as poly(N-isopropylacrylamide) (pNIPAM) copolymers, have been demonstrated to form a robust gel matrix at physiological temperatures, while still reserving the responsiveness to temperature. Extensive *in vitro* adhesion studies show that the interfacial seed layer greatly increases the adhesive strength between tissue surface and polymer matrix, with the adhesion strength on the order of 100 J m$^{-2}$ when skin tissue is adhered. Easy detachment can be induced by changing the temperature which causes the loss of cohesive strength of the polymer gel by marked softening or dissolution. The in-situ adhesion of our adhesive formula to ocular surface is realized in an *in vivo* rabbit model, and the adhesive can be easily released by rinsing with cold water. The design is low-cost, easy to fabricate, and shows great potential for application as point-of-care medical devices.

**COLL 87**

**State of nanoparticle active tumour cell targeting**
Coating the nanoparticle surface with cancer cell recognizing ligands is expected to facilitate specific delivery of nanoparticles to diseased cells in vivo. While this targeting strategy is appealing, no nanoparticle-based active targeting formulation for solid tumor treatment had made it past phase III clinical trials. Here, we quantified the cancer cell-targeting efficiencies of Trastuzumab (Herceptin) and folic acid coated gold and silica nanoparticles in multiple mouse tumor models. Surprisingly, we showed that less than 14 out of 1 million (0.0014% injected dose) intravenously administrated nanoparticles were delivered to targeted cancer cells, and that only 2 out of 100 cancer cells interacted with the nanoparticles. The majority of the intratumoral nanoparticles were either trapped in the extracellular matrix or taken up by perivascular tumor associated macrophages. The low cancer cell targeting efficiency and significant uptake by noncancer cells suggest the need to re-evaluate the active targeting process and therapeutic mechanisms using quantitative methods. This will be important for developing strategies to deliver emerging therapeutics such as genome editing, nucleic acid therapy, and immunotherapy for cancer treatment using nanocarriers.

Coll 88

Protein nanoparticles as multifunctional drug delivery carriers

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Precise control of the physical and biochemical properties of nanoparticle-based drug delivery vehicles is a prerequisite for effective transport of drugs across a range of biological barriers. To date, the range of biodegradable macromolecular systems with appropriate biocompatibility, low levels of immunogenicity and extended structural stability that can be prepared at scale remains rather limited. Towards that end, nanoparticles comprised of protein/polymer conjugates offer a range of unique features, such as biodegradability and extended in vivo stability, active targeting and stimuli-responsiveness, or the potential for delivery of small-molecule drugs and biopharmaceuticals. Electrohydrodynamic (EHD) co-jetting, an adaptive manufacturing process that involves transferring two or more capillary needles in a side-by-side configuration, can be used to create a wide range of multicompartmental protein/polymer nanoparticles. The protein nanoparticles combine the processability of synthetic polymers with the biological properties of proteins. In the context of glioblastoma multiforme, protein nanoparticles have been devised that enable systemic delivery of RNAi to intracranial brain tumor. Protein nanoparticles that can enable controlled release of multiple cancer drugs from the same nanoparticle will also be discussed.

Coll 89
Ultrafast single micron to sub-micron particle detection method based on a half-bowtie coplanar waveguide

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From a physics-tech perspective one of the truly high-impact inventions in the field of bio-physics is the Coulter-counter. To this date it is found in applications worldwide and is being extended to counting sub-micron particles, strands of DNA, and even single molecules. By now the topic forms a research field in its own right and is part of many clinical applications due to its simplicity and high-throughput capabilities. The principle of operation is straightforward: a pore is embedded in a thin membrane, separating two reservoirs filled with electrolyte solution. A voltage across the membrane leads to an ionic current flow through the pore. Depending on the pore diameter this current ranges from nano-, for micron sized pores, to pico-amperes for nanopores. When a particle translocates through the pore the open pore current is altered by the presence of this particle because it partially blocks the ion flow and thus increases the resistivity of the pore. We present an ultrafast single micron to sub-micron particle detection method based on a half-bowtie coplanar waveguide. The method is capable of resolving the translocation of these particles at a bandwidth greater than 30MHz and has the potential to trace charge distribution inside of cells. We compare experimentally the simultaneous use of our radio-frequency technique with conventional DC based resistive pulse recordings and find that our method has a throughput that is enhanced by two orders of magnitude. The technique incorporates a microfluidic circuit and has potential to be employed for screening nano-particles and biopolymers such as DNA at frequencies in excess of 1 GHz.

COLL 90

How does nano-silver get inside bacteria? Mechanistic studies using AgAu alloy nanoparticles

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Silver nanoparticles are frequently used to fight infections derived from multiresistant bacteria, however the toxicity to cells and hence the limited therapeutic window still
restricts their application. In addition, the mechanism of silver-derived toxic and antimicrobial is to date not fully understood and furthermore, studies on the uptake of Ag nanoparticles by bacteria are rare. In this work, we used gold-silver alloy nanoparticles as alternative antimicrobial agents. The particles were fabricated by pulsed laser ablation in liquids, a technique which does not require any artificial organic stabilizers and hence may avoid potential toxic cross-effects from ligands. We could show that the composition of the AgAu particles could be controlled by the composition of the ablated targets and the generated particles exhibited a fully homogeneous elemental distribution (probed by EDX line scans) and a crystal structure identical to the used targets (determined by XRD). In biological assays with oocytes, bacteria and human fibroblasts we found a non-linear decrease of the antimicrobial activity with increasing gold molar fraction, probably attributed to an inhibition of silver dissolution from the nanoparticles by the more noble metal gold. Furthermore, we found that the cellular uptake of gold and silver nanoparticles by oocytes is material dependent. Consecutively, we studied the cellular uptake of AgAu alloy nanoparticles by the model bacterium S. aureus. Interestingly, we found only small particles inside the bacteria, however, these were significantly more silver rich than those originally exposed to the cell. Based on these findings we could conclude that these intracellular silver-rich particles were probably formed by dissolution and intracellular reduction of the silver ions.

COLL 91

Nanotoxicology: Exploring nanoparticle-model membrane interactions

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Nanoparticle-cell interactions are important for determining the safety of nanoparticles to humans and the environment. Such interactions are also the basis of many critical applications, such as drug or nutrient delivery and diagnostics. In this research, we focus on a unique mechanism of cytotoxicity, namely, membrane destabilization, which is principally dependent on the nanoparticulate nature of the material rather than on the molecular properties of the material. We construct supported lipid bilayers (SLB) of L-α-phosphatidylcholine on a quartz crystal and employ that as a model cell membrane to interrogate the membrane interactions with nanoparticles. The interactions of gold nanoparticles of different sizes with the SLB were investigated using the Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) technique. The nanoparticles were tested in their citric acid stabilized state as well as in the presence of a synthetic polymer and also samples of natural organic matter. The observed interactions of the nanoparticles with the lipid bilayer, or the lack thereof, are interpreted using a simple phenomenological model of membrane adhesion and folding, resembling endocytic transport processes. The results call for a new paradigm in nanotoxicology studies in
the sense that neither the nanoparticle characteristics not the cell type may be adequate predictors of cytotoxicity without accounting for the environment in which they are present.

**COLL 92**

**Multi-hierarchically profiling the biological effects of various metal-based nanoparticles in macrophages under low-exposure doses**

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Thus far, tremendous efforts have been made to understand the bio-safety of metal-based nanoparticles (MNPs). Nevertheless, most previous studies focused on specific adverse outcomes of MNPs at unrealistically high concentrations with little relevance to the National Institute for Occupational Safety and Health (NIOSH) exposure thresholds, and failed to comprehensively evaluate their toxicity profiles. To address these challenges, we here endeavored to multi-hierarchically profile the hazard effects of various popularly used MNPs in macrophages under low exposure doses. At these doses, no remarkable cell viability drop and cell death were induced. However, cellular anti-oxidant defense system was seen to be initiated in cells by all MNPs even at these low concentrations, albeit to a differential extent and through different pathways, as reflected by differential induction of the anti-oxidant enzymes and Nrf2 signaling. Regarding inflammation, rare earth oxide nanomaterials (REOs) except nCeO$_2$ greatly increased IL-1β secretion in a NLRP3 inflammasome-dependent manner. By contrast, six REOs, AgNP-5nm, nFe$_2$O$_3$, nFe$_3$O$_4$ and nZnO were found to elevate TNF-α concentration through post-transcriptional regulation. Moreover, all MNPs except nCeO$_2$ drastically altered cellular membrane/cytoskeleton meshwork, but leading to different outcomes, with condensed cellular size and reduced numbers of protrusions by REOs and elongated protrusions by other MNPs. Consequently, REOs (e.g. nDy$_2$O$_3$ and nSm$_2$O$_3$) impaired phagocytosis of macrophages, and other MNPs (such as AgNP-25nm and nZnO) reversely enhanced macrophagic phagocytosis. Alterations of membrane and cytoskeleton meshwork induced by these MNPs also caused disordered membrane potential and calcium ion flux. Collectively, our data profiled the biological effects of different MNPs in macrophages under low exposure doses, and deciphered a complex network that links multi-parallel pathways and processes to differential adverse outcomes.

**COLL 93**

**Degradation of hybrid nanoparticles**

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Enzymes can digest the organic surface coating around nanoparticles, which involves the surface chemistry of the nanoparticles which warrant for their colloidal stability, as adsorbed proteins. By labelling different compounds of the hybrid nanoparticles with fluorophores their intracellular degradation can be following in vitro. With restrictions quantitative analysis is possible, which will be discussed.

**COLL 94**

**Human serum protein coronas greater alter interactions between nanoparticles and a model red blood cell membrane**

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Nanoparticles (NPs) in contact with biological fluids are immediately coated by a protein corona (PC), composed of hard (strongly bounded) and/or soft (loosely associated) protein layers. The PC governs the biological ‘identity’ of a NP and represents the actual nano-interface that is presented to and interacts with cellular membranes. Understanding such interactions can be used to design nanomaterials with controlled surface characteristics in a biological environment. In this regard, lipid monolayers employed as model membranes have been extensively used to examine interactions between bio-membranes and NPs. In this work, we combined Langmuir Blodgett technique with hyperspectral and Brewster Angle microscopy to investigate how the NP-cell membrane interactions are modulated by the presence of a protein (human serum albumin), either free in the environment or included in the hard and soft coronas, and to explore their effects on the formation and structure of lipid domains. Our results show that the inclusion of 100 nm polystyrene (PS) nanoparticles within a monolayer does not affect the monolayer lipid packing and phase state. Complexation of the PS NPs with proteins promotes their attachment to the lipid monolayers. PS NPs-hard corona (HC) complexes cause lipid extraction at high monolayer surface pressure (30 mN/m ) and lead to the modification of the monolayer phase behavior with hindering of growth of solid domains, increasing of the monolayer resistance to compression, and lowering of the collapse pressure. We also found that NPs-soft corona (SC) complexes, representing the prevailing structure that would be present biologically, induced greater changes in lipid monolayer structure than the NPs alone at the same concentration. Compared to NP-HC complexes, NP-SC complexes yield more disordered structure in monolayers with less cohesion between the lipid molecules.

**COLL 95**

**Ionically crosslinked polymers for antimicrobial textiles**

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Ionically crosslinked polymers (ICP) are a new class of emerging materials with unique properties. These ionically crosslinked materials can be simply synthesized by the thermal Huisgen 1,3-Dipolar Cycloaddition of alkynes to azides with in situ quaternization yielding triazolium based cross-link points with iodide as their counter anion in one step. These charged crosslinked polymers coupled with their ease of synthesis, and inherent properties resulting from the charge nature of these materials makes them ideal for a variety of applications including membranes for gas separation, and solid electrolytes for batteries. The presence of iodide moiety in ICP makes them ideal for anti-microbial application. Herein, we will present our recent work on the modification of various textiles and show improved anti-microbial properties.

**COLL 96**

**Preparation of functional polymers and fibers through controlled radical graft polymerization processes**

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Radical graft polymerization is uniquely applicable in chemical modifications of most synthetic polymers and fibers, and the reactions can be implemented at different stages of polymer processing or even fiber extrusion. In this presentation, a few examples of successful chemical modifications of cellulose, olefin, polyamide, and polyester are discussed by employing novel control processes in carrying out the reactions. First, cellulose fibers can be modified as fiber or fabric forms by graft radical polymerization processes. On the other side, olefin polymers such as polypropylene, polyethylene, and their copolymers can undergo graft polymerization modifications in reactive extrusion processes. The reactions occur in the extruders. Polyamide and polyester fibers can be surface modified using radical initiated graft polymerization by having a well-controlled reaction system using Hanson solubility parameters as a tool. The reaction is currently conducted at a finishing process but can be implemented in fiber drawing or texturing processes. Biocidal fibers and fabrics could be successfully produced by these processes and will be examples presented.

**COLL 97**
3-Mercapto-1,2-propanediol modified robust polyester nonwoven for stabilization of zero-valent iron nanoparticles for multifunctional application

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Highly oxidation tendency of zerovalent iron nanoparticles limits its various practical applications. In this work, stabilization of zerovalent iron nanoparticles (nZVI) in 3-Mercapto-1,2-propanediol (α-thioglycerol, α-TG) modified polyester nonwoven (PN) for improved catalytic and antibacterial application has been studied for the first time. Changes in wettability as well as structural, morphological, thermal and catalytic properties of the resulting PN/α-TG/nZVI material were investigated by scanning electron microscopy, energy dispersive X-Ray, zeta potential measurements, thermogravimetric analysis, differential scanning calorimetry, fourier transform infrared and UV–visible spectroscopies. Prior to functionalization, hydrophilic functional groups have been introduced in PN surface by air atmospheric plasma treatment. Iron nanoparticles were immobilized by α-thioglycerol on the polyester fibers with a multimeter particle size. α-TG stabilized nZVI by reducing the tendency of easy oxidation. nZVI insertion resulted in high thermal stability of PN. As an application, PN/α-TG/nZVI exhibited an excellent catalytic activity in the reduction of 4-nitrophenol with appreciable recyclability. The results further demonstrate that PN/α-TG/nZVI can be employed not only for toxic compounds removal but also to inhibit the growth of bacteria at normal conditions which herein open new prospects for concrete industrial applications of nZVI based multifunctional systems.

COLL 98

Perfluoropolyether-based molecular bottlebrush as water/oil repellent additive for fiber forming thermoplastics

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For decades, water and oil repellency of fiber forming thermoplastics has been achieved with introduction of long-chain perfluoroalkyl substances and moieties (PFASs, C_nF_{2n+1}, n ≥ 7). However, they have been phased out of industrial production and textile applications due to their bioaccumulative and toxicological impact. To this end, we synthesized novel perfluoropolyether (PFPE)-based methacrylate monomer (FM) by reacting PFPE-based alcohol with methacryloyl chloride. The resulting monomer was polymerized radically to obtain PFPE-based fluorinated polymer (PFM). The polymer does not possess long-chain perfluoroalkyl segments and has structure of molecular bottlebrush where relatively long side chains are anchored to the linear backbone at
high grafting densities. In our study, the polymer was used as a low-surface energy additive for modification of industrial fiber forming thermoplastics. Specifically, the surface properties such as wettability and morphology of PFM/thermoplastic polymer films were studied using contact angle measurements and atomic force microscopy. It was found that PFM, when added to nylon 6, polyethylene terephthalate (PET), and poly(methyl methacrylate) (PMMA) films, readily migrates to the film surface and brings significant water and oil repellency to the thermoplastic boundary. The addition of this PFM polymer to thermoplastics, even at quite low concentration, allows the polymer films reaching a level of oil wettability and surface energy lower than that of polytetrafluoroethylene (PTFE/Teflon). We associate this efficiency of the polymer in achieving high water and oil repellency with its ability to form molecular bottlebrush nanoscale layer on polymer film surfaces. Therefore, the polymer can be considered as safer replacement for additives containing long-chain perfluoroalkyl substances.

![Hexadecane (oil) contact angle for PFM/nylon 6 films of different PFM content before and after annealing.](image)

COLL 99

Environmentally-friendly superhydrophobic and superoleophobic fabrics prepared from water-based suspensions
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Superhydrophobic and superoleophobic textiles have been the focus of much attention owing to their attractive properties such as water- and stain-resistance. However, the improvement of currently existing methodologies and the development of new coating strategies are still needed with the aim of reducing the complexity of preparation and application, of decreasing cost, and of limiting environmental issues. Usually, the application of super-hydrophobic/oleophobic coatings involves multiple and often complex steps, and the use of organic solvents. Additionally, currently existing superhydrophobic and superoleophobic formulations mostly employ perfluorinated compounds that can degrade into perfluorooctyl oligomers which are harmful to the environment and to living organisms, and are being banned in the United States and the European Union. In this context, we have developed water-based green methodologies to treat fabrics with superhydrophobic and superoleophobic formulations, devoid of perfluoroheptyl and perfluorooctyl (or longer) derivatives, which can be easily applied on fabrics (and other substrates) in one single step by dip-coating or spray-coating. We quantitatively correlate the wetting of the fabrics by water and oil to their roughness, which arises from fabric texture and the addition of silica nanoparticles, and investigate how crosslinking can improve the washing and chemical resistance of the fabrics. Thereby, we demonstrate that our water-based formulations provide a practical solution to an acute environmental issue.

**COLL 100**

**Superhydrophilic, wrinkle-free cotton fabrics via plasma and nanofluid treatment**

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For more than two decades in the apparel industry, there has been consistently high demand of wrinkle-free cotton garments for easy care and comfort. Conventional wrinkle-free finishing is based on the crosslinking reaction between molecular chains of cellulose via formaldehyde derivatives such as dimethyldihydroxyethyleneurea (DMDHEU). DMDHEU reacts with the hydroxyl (-OH) groups in cotton, which increases wrinkle-resistance and shape retention. However, the finishing reduces the hydrophilicity of the fabric due to the reduction of the number of OH groups; consequently, the moisture sorption capacity and wicking properties are reduced, resulting in a deterioration in the comfort of cotton fabric. Therefore, recovering the hydrophilicity of wrinkle-free finished cotton has very significant practical value.

We demonstrate in this study, a wrinkle-free, superhydrophilic, cotton fabric (contact angle 0°) by attaching specially engineered nanoparticles to plasma pre-treated cotton fabric. Because of their charged nature, the nanoparticles are firmly anchored on the fabric via electrostatic interactions; the surface structures were confirmed by image and
The durability of wetting behavior and wrinkle-free property of the NP-coated fabrics was evaluated via aging, laundering, and abrasion tests. The strongly attached coatings are stable maintaining their superhydrophilic nature even after 60 days’ aging and 50 laundering cycles. The nanoparticle-coated fabric also combines superhydrophilicity with very good wrinkle-recovery property, tensile strength and abrasion resistance (25,000 abrasion cycles) performance.

COLL 101

Microencapsulation of natural insect repellents for protective coatings on fabrics

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Vector-borne diseases—such as malaria, zika, Keystone Virus, and elephantiasis—are a plague on mankind. Typically, these diseases are transmitted by insect bites from mosquitoes or flies. Because of this, much research has been conducted into providing more convenient and effective methods of protection from insect bites. To this end, attempts have been made to incorporate safer insect repellents into wearable clothing and fabrics. However, simply coating an insect repellent onto fabric leaves it vulnerable to evaporation and loss during washing. In this research, natural insect repellents such as citronella oil or geraniol are incorporated into reservoir and matrix microcapsules consisting of gelatin/gum arabic and gelatin, respectively. The microcapsules or matrix microcapsules are crosslinked and coated onto NYCO fabric. The morphology of the coated fabrics is studied using optical microscope imaging and SEM. The release rate is determined using a variety of techniques. The effect of degree of crosslinking on repellent release rate and durability during washing is being studied.

COLL 102

Interfacial self-assembly of hierarchically structured nanoparticles with photocatalytic activity

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Design and engineering of the size, shape, and chemistry of photoactive building blocks enable the fabrication of functional nanoparticles for applications in light harvesting, photocatalytic synthesis, water splitting, phototherapy, and photodegradation. Here, we report the synthesis of such nanoparticles through a surfactant-assisted interfacial self-
assembly process using optically active porphyrin as a functional building block. The self-assembly process relies on specific interactions such as π–π stacking and ligand coordination between individual porphyrin building blocks. Depending on the kinetic conditions, resulting structures exhibit well-defined one- to three-dimensional morphologies such as nanowires, nanoctahedra, and hierarchically ordered internal architectures. At the molecular level, porphyrins with well-defined size and chemistry possess unique optical and photocatalytic properties for potential synthesis of metallic structures. On the nanoscale, controlled assembly of macrocyclic monomers leads to formation of ordered nanostructures with precisely defined size, shape, and spatial monomer arrangement so as to facilitate intermolecular mass and energy transfer or delocalization for photocatalysis. Due to the hierarchical ordering of the porphyrins, the nanoparticles exhibit collective optical properties resulted from coupling of molecular porphyrins and photocatalytic activities such as photodegradation of methyl orange (MO) pollutants and hydrogen production. The capability of exerting rational control over dimension and morphology provides new opportunities for applications in sensing, nanoelectronics, and photocatalysis.

**COLL 103**

**Photophysics and electronic structure of metal-organic frameworks**

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Self-assembled materials such as metal–organic frameworks (MOFs) could add a new dimension to a wide number of applications including supercapacitors, electrodes, or thermoelectrics. From this perspective, the understanding and tailoring of the electronic properties of MOFs are key fundamental challenges that could unlock the full potential of these materials. For instance, materials with a predesigned pathway for ET can address the urgent needs in fast enhancement of material performance in areas ranging from optoelectronic devices to photocatalytic systems and, thereby, drastically modify the existing energy and material landscape. MOFs have significant advantages to achieve directional ET. For instance, they provide a high level of control for chromophore arrangement, structural parameters, and photophysical properties, through rational chromophore design and synthetic conditions unprecedented for large light-harvesting ensembles and extended structures. In this presentation, mechanistic and structural aspects of directional energy transport will be discussed on the examples of photochromic, fulleretic, and biomimetic systems in order to harness MOFs as a versatile platform for energy utilization enhancement. These studies unveil the possible pathways for transforming the electronic properties of MOFs from insulating to semiconducting, as well as provide a blueprint for the development of hybrid porous materials with desirable electronic structures.

**COLL 104**
Structural and mechanical properties of self-supporting covalent organic framework membranes obtained via two different preparation routes

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Crystalline materials with high nanoscale porosity have the potential applications in a wide range of fields such as catalysis, gas storage, filtration, and energy conversion and storage. Covalent organic frameworks (COFs) are a customizable and predictable class of materials with attractive crystallinity and porosity. When synthesized in films with nano- or micron-scale thicknesses, COFs become viable candidates for applications in engineered systems, e.g., flow-through filtration. However, moving to these applications requires the development of an understanding of the mechanical properties of these COF membranes, which are key to their successful use in applications, particularly where the films may be required to self-support.

Here, we present our work on rigid, freestanding COF-1 membranes with micron-scale thicknesses that have been synthesized using two different routes: a room temperature solvent vapour annealing approach and thermal annealing. We have compared the membranes produced from these two procedures using a range of techniques, including microscopy (optical, scanning electron and atomic force), FTIR, x-ray diffraction, and gas adsorption. We have also measured the Young’s modulus of the films using nanoindentation, providing new insight into COF mechanical properties. These measurements allow us to begin considering how free-standing COF membranes might be incorporated into applications.

COLL 105

Rigid rod vs semiflexible chain construction through connection of computationally designed coiled coil peptides using Thiol-Michael click reaction

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Peptides that oligomerize into robust coiled coils have emerged as promising candidates for constructing self-assembled nanomaterials that display designed, hierarchical organization of the coiled coil bundles. Using an optimized computational prediction algorithm, artificial coiled coils that consist of four identical α-helical peptides were designed such that the 30 amino acid peptides pack in an antiparallel fashion within the individual coiled coil bundle. Chemical modification of the peptide N-termini to
incorporate an extra cysteine or maleimide functional group resulted in coiled coil bundles decorated with either four thiols or four maleimide moieties (two at either bundle end due to antiparallel peptide packing within bundles). These modified bundles were subsequently covalently linked together using different linker types via Thiol-Michael click reactions to build polymers of coiled coils, or "bundlemers", that were readily viewable under the Transmission Electron Microscope (TEM). Specifically, a short rigid linker between bundles resulted in formation of rigid rods of coiled coils displaying a persistence length greater than tens of microns while a flexible linker between bundles resulted in semiflexible fibers with a shorter persistence length. Also, via computational design, the net charge on the bundle-forming peptides was altered (-8 to +8) such that the resulting bundlemers carried different net charge densities and local charge patchiness. The differences in the assembled nanostructures driven by peptide sequence manipulation are encoded in their respective Small-Angle Neutron Scattering or X-ray Scattering (SANS, SAXS) curves which further confirmed the success of the computational design strategy and hybrid assembly pathway. Furthermore, concentrated solution of rigid rods displayed liquid crystallinity wherein the birefringent texture was responsive to the presence of sodium chloride salt, which indicates an electrostatically-driven interaction and assembly of the coiled-coil based rigid rods in solution. This result is supported by scattering of the rod solutions under different solution conditions, and we show that such inter-rod interactions are readily tunable by sequence manipulation of the coiled coil forming peptides.

COLL 106

Locking-in 1-dimensional π-conjugated superstructures to regulate the formation of well-defined nanoscale objects

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Self-assembled organic architectures are fragile compositions where minor changes in temperature, solvent dielectric, and building-block concentration can trigger the dismantlement of superstructures with a concomitant loss of the emergent properties associated with them. To tackle this challenge, we are currently developing molecular strategies to lock-in 1D π-conjugated superstructures. Our goal is to create well-defined nanoscale platforms with which to unravel structure-function properties that remain elusive with current self-assembly methodologies. We will introduce the design principles to reticulate 1D supramolecular polymers following a 1,3-dipolar cycloaddition “click-chemistry” (Fig. 1A). While ground-state electronic absorption spectra (Fig. 1B-C) reveals the formation of robust superstructures, atomic force microscopy (Fig. 1D-E) and transmission electron microscopy confirmed that organic nanomaterials are best characterized by a nanowire morphology. As these well-defined nanoscale objects are soluble in aqueous media, conventional gel permeation chromatography techniques are utilized to sort them by size. Investigation of the electronic properties of length-sorted nanowires exploiting electrochemical measurement methods reveals a non-negligible
stabilization of the energy of the conduction band with respect to that of parent, non-polymerized self-assemblies. It is important to note that the presented strategy opens new avenues to not only capture conformation of supramolecular assemblies but also to enforce the formation of emergent electronic properties not accessible in pristine, non-covalent assemblies.

Figure 1. A) Schematic illustration of the designed strategy to lock-in superstructure conformation using amphiphilic diazide linkers. (B, C) Spectroscopic evidences of superstructure locking. In contrast to unlocked superstructures that dismantle in a good solvent (B), locked-in superstructures (nanowires) evidence spectroscopic signatures (C) reminiscent of solubilized semiconducting materials. (D, E) AFM images that highlight the solid-state morphology of drop-casted organic nanowires from parent H2O and MeOH solution.

Coll 107

Controllable, wide-ranging n- and p-doping of monolayer transition-metal disulfides and diselenides

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Two-dimensional (2D) materials including graphene and transition metal dichalcogenides (TMDs) have been intensively explored for fundamental research and
technological applications. The ultrathin nature and large surface area of 2D materials enable their optical and electrical properties to be tuned through surface modification. In this study, redox-active molecules were introduced onto the surface of 2D materials to achieve strong and nondestructive n- and p- doping effects. A series of monolayer TMDs, including MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$, were tested. Doping was achieved by exposing the TMD surface to solutions of pentamethylrhodocene dimer as the molecular reductant and “Magic Blue,” [N(C$_6$H$_4$-p-Br)$_3$]SbCl$_6$, as the molecular oxidant. The degree of doping can be finely controlled by the choice of dopants, treatment time, and the concentration of doping solution. Notably, current-voltage characteristics of TMD-based field-effect transistors show that, regardless of their initial transport behavior, all four TMDs can be used in either p- or n-channel devices when appropriately doped. Detailed physical characterizations were conducted to study the doping effect. Photoluminescence (PL) properties of the doped monolayer TMDs were measured; for all four materials the PL intensity is enhanced with p-doping but reduced with n-doping. X-ray photoelectron spectroscopies (XPS) was performed to investigate the impact of doping on the TMDs chemical structure and energy levels. The coverage of absorbed doping product was also calculated based on the XPS data. Estimates of changes of carrier density from electrical, PL, and XPS results were compared. In summary, this technique provides a simple yet effective route to tailor the band structure of the 2D materials and control the resulting electrical and optical properties.
Over the past decade, comprehensive investigations have been conducted to develop two-dimensional (2D) materials to harness their excellent and unprecedented properties such as high electrical conductivity, optical transparency, mechanical strength, and flexibility. This necessitates developing means for their mass production. This study details a newly conceived compressible flow exfoliation method for producing 2D h-BN nanomaterials.
nano sheets using a multiphase flow of 2D layered materials suspended in a high pressure gas undergoing expansion. A supersonic flow is achieved in a needle valve and the residence time of the materials were calculated to be 200 micro seconds. The expanded gas-solid mixture is sprayed in a suitable solvent, where a significant portion (up to 10%) of the initial hexagonal boron nitride (h-BN) material is found to be exfoliated with a mean thickness of 4.2 nm. Moreover, 43% of the exfoliated h-BN were found to be 10 layers or less thick while having a mean flake length of 276 nm and concentration of 0.22 mg/mL in Isopropyl Alcohol (IPA) after centrifugation. Shear-induced exfoliation occurs due to the high velocities that expanding and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate (γ>10^5 s^-1) experienced by the bulk h-BN particles. Decoupling of exfoliation step from liquid suspension step leads to a very stable suspension of h-BN nano sheets into IPA for a long time (6 months). The CFE method has significant advantages over current 2D material exfoliation methods, such as chemical intercalation and exfoliation, and liquid phase shear exfoliation, with the most obvious benefit being the fast, continuous nature of the process. Other advantages include environmentally friendly processing, reduced occurrence of defects, separation of the exfoliation from the suspension step and versatility to be applied to any 2D layered material using gaseous medium.

**COLL 109**

**Fluid-like reconfigurable graphene matrix with superlubricity**

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Advanced functional graphenes provide unique opportunities for achieving unusual physical and chemical properties to meet the high-performance demands for next generation technologies. The development of frictionless coating, defined by coefficient of friction (COF) lower than 0.01, is essential for the sustainability and achieving higher mechanical performance. Although intrinsic graphene has a desirable incommensurability in its lattice plane with Au(111), promoting stable incommensurate contact at macroscale edges is still challenging. To overcome these macroscopic limitations, we designed a dynamical graphene matrix to produce stable superlubricity for real world applications. First, we exfoliated single layer functionalized graphene with 3,5-dinitrophenyl groups from a Hyperstage-1 graphite intercalation compound (GIC). The functionalized graphene shows exceptional dispersibility (0.24 mg ml^-1) in N,N-dimethylformamide (DMF) and reacts with nucleophilic primary amines to form reversible Meisenheimer complexes. Second, to create a new superlubricant material, we designed the reconfigurable graphene matrix, incorporated with structurally rigid triptycene molecular cores, that shows superlubricant behaviors. The dynamic reactivity of the functionalized graphene and the rigid frame of triptycene produces unique incommensurate interfaces under mechanical sliding deformation. We experimentally show that the fluid-like graphene matrix produces stable tribo-layers and an ultralow...
COF (~0.008) against the diamond-like-carbon (DLC). The structural reconfiguration of the graphene matrix provides a new novel pathway to achieve robust superlubricity.

COLL 110

Dispersion, characterization, and diffusion of boron-nitride nanotubes in water

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Boron-nitride nanotubes (BNNTs) are one dimensional tubular structures with the morphology of rolled hexagonal boron-nitride sheets. The structure of BNNTs is similar to that of carbon nanotubes (CNTs), but with alternate boron and nitrogen atoms forming the structure instead of carbon atoms. BNNTs and CNTs have high tensile strength, high thermal conductivity, and self-assemble in big bundles that make them difficult to disperse in aqueous solution. In contrast to CNTs, BNNTs are wide band semiconductors (5.5 eV) and present high chemical and thermal stability. In this research we investigated the dispersion of BNNTs in aqueous solution using different surfactants. The mass conversion (% of BNNTs left in solution after dispersion) was calculated using thermal gravimetric analysis. The individualization of the BNNTs was studied using TEM and AFM, and the stability of the solutions was assessed by UV-Vis absorption spectrometry, dynamic light scattering (DLS) and zeta-potential. Furthermore, we studied the diffusion of BNNT using fluorescence microscopy by dispersing the nanotubes using a special fluorescent surfactant. Diffusion and rotational correlation times were obtained as a function of BNNT length and compared to a rigid rod model. These results has led to a better understanding of BNNT dispersion, stability and characteristics, which is a necessary step for taking advantage of the outstanding properties of these nanomaterials.

COLL 111

Temperature-induced transformation of amphiphilic thermo-sensitive hyperbranched poly(ionic liquid)s

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We demonstrated the assembly of amphiphilic thermo-sensitive hyperbranched
poly(ionic liquid)s (HBP-PILs) with asymmetric peripheral branched compositions at air-water interfaces as a function of surface pressure and temperature. We found that the HBP-PILs consisting of 24 hydrophobic N-octadecylisocyanate arms and 8 hydrophilic poly(N-isopropylacrylamide) (PNIPAM) macrorations with carboxylic terminal groups formed disk-like and long cylindrical micelles in solid and liquid 2D phases on Langmuir isotherms, respectively. These HBP-PILs also exhibited LCST-type phase transition even when confined to interfaces due to the presence of PNIPAM macrorations in the water subphase. Increasing temperature above LCST resulted in the collapse of PNIPAM macroration chains, promoting the reorganization from a network of cylindrical micelles to a network of collapsed aggregates. These findings can be applied in the development of new hierarchical building blocks based on poly(ionic liquid)s with diverse, stimuli-responsive assembly behavior.

COLL 112

Counting charges on surface-bound peptides

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Quantifying the number of charges on peptides bound to interfaces requires reliable estimates of (i) surface coverage and (ii) surface charge, both of which are notoriously difficult parameters to obtain, especially at solid/water interfaces. Here, we report the thermodynamics and electrostatics governing the interactions of L-lysine and L-arginine octamers (Lys8 and Arg8) with supported lipid bilayers prepared from a 9:1 mixture of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and 1,2-dimyristoyl-sn-glycero-3-phosphorylglycerol (DMPG) from second harmonic generation (SHG) spectroscopy, quartz crystal microbalance with dissipation (QCM-D) and nanoplasmonic sensing (NPS) mass measurements, and atomistic simulations. The combined SHG/QCM-D/NPS approach provides interfacial charge density estimates from mean field theory for the attached peptides that are smaller by a factor of approximately two (0.12 +/- 0.03 C m^-2 for Lys8 and 0.10 +/- 0.02 C m^-2 for Arg8) relative to PLL and PLR. These results, along with atomistic simulations, indicate that the surface charge density of the supported lipid bilayer is neutralized by the attached cationic peptides. Moreover, the number of charges associated with each attached peptide is commensurate with those found in solution; that is, Lys8 and Arg8 are fully ionized when attached to the bilayer. Computer simulations indicate Lys8 is more likely than Arg8 to “stand-up” on the surface, interacting with lipid headgroups through one or two sidechains while Arg8 is more likely to assume a “buried” conformation, interacting with the bilayer through up to six sidechains. Analysis of electrostatic potential and charge distribution from atomistic simulations suggests that the Gouy-Chapman model widely used for mapping the measured surface potential to surface charge is semi-quantitatively valid; despite considerable orientational preference of interfacial water, the apparent dielectric constant for the interfacial solvent is about 30, due to the thermal fluctuation of lipid-water interface.
Parent Zn and Ni metalloporphyrins form bilayers at the air/water interface

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The behavior of unsubstituted Zn and Ni metalloporphyrins at the air/water interface in a Langmuir-Blodgett trough has been investigated by examination of compression isotherms, electronic spectroscopy, grazing incidence X-ray diffraction, and X-ray reflectivity. It has been concluded that both metalloporphyrins form bilayers composed of two parallel square arrays of 11.2 Å unit cell length, mutually displaced by about 1/4 of the diagonal, placing the metal atoms of one layer above the pyrrole rings of the other.

On-surface assembly and reactivity of oligo/polythiophenes

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Thiophene-based building blocks have played a dominant role in establishing the field of organic electronics.[¹] It is hard to find any efficient semiconducting polymer that would have no thiophene rings in its structure. At the same time, the presence of sulfur in the molecules, significantly affects and complicates their interaction with the surfaces. In this talk I will summarize our decade long scanning probe microscopy studies of on-surface self-assembly[²] and reactivity[³] of thiophene-contained π-conjugated molecules and present some new results showcasing the behavior of high S/C ratio molecules on surfaces of different reactivity (HOPG/Au/Ag/Cu).

Standing, lying, and sitting: Unique properties of diyne phospholipid striped phases in templating inorganic and organic nanomaterials

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A surprisingly broad array of problems in modern materials chemistry relate to creating interfaces with two distinct, well-structured chemical environments at near-molecular scales. For instance, positioning nm-wide metal and semiconductor features with a pitch
of 5-7 nm in a structured matrix represents a central requirement for next-generation electronic devices. 2D materials noncovalently functionalized with striped phases of amphiphiles present functional patterns at scales relevant for templating deposition of other materials for device applications. We find that assembling striped phases from diyne phospholipids creates interfaces with very different properties than simple dyinoic acids or diyne amines. In part, this difference appears to arise from strong, orientable headgroup dipoles found in phospholipid headgroups, which confer function based on collective interactions similar to those in the cell membrane periphery. We will discuss the relationship between structure and function at striped phospholipid interfaces, and useful material properties that emerge from the unusual surface chemistry; these include assembly of inorganic nanocrystals and crystallization of functional organic molecules.

**COLL 116**

**Leveraging a step-wise, sequence-specific synthesis of shape-persistent macrocycles to control hierarchical self-assembly on surfaces**

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Hierarchical assembly provides a route to complex architectures when using building blocks with recognition elements that are strong and structurally well-defined. For this purpose, shape-persistent macrocycles offer distinct advantages: the recognition elements encoded into their rigid inner and outer surfaces are reliably retained and displayed. Tricarbazole (tricarb) macrocycles are exemplary. These macrocycles possess electropositive cavities for anions, hydrogen bonding motifs for complementary contacts, and have large π-faces for stacking. Building on this macrocycle framework, we utilize a step-wise synthesis to program peripheral alkyl units and other functional groups in order to probe their impact on the two-dimensional, ordered tricarb assemblies. This 2D assembly was investigated at the solution-surface interface using scanning tunneling microscopy. The work presented here demonstrates the power granted by sequence-specific syntheses in the study and control of self-assembly on surfaces.

**COLL 117**

**BioNanoarchitectonics and the dynamics of alive functional surfaces**

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Nature masters function at the nanoscale by controlling the structure-function code through a combination of covalent and supramolecular forces. I define BioNanoarchitectonics as a path to unravel nature’s protocols to design hierarchical materials from molecular building blocks that can self-assemble with predictable shapes and functions.
- How does information coded into structure transfers from single molecules to complex 2D assemblies? Can we revert the structure-function equation and looking at a function in biology use simple building blocks to code function into structure?

- What is the limit of biomimetics at the nanoscale and how do we interface the Nano to the Macro world? Can we go beyond the static atomistic view and understand dynamics and reactivity? Could BioNanoarchitectonics be a route to use the design principles of nature to create bioinspired catalysts and smart materials?

In this talk, I will share my vision and describe the systems we explore to address these questions. Using in-operando scanning probe microscopies and electrochemical techniques to study the influence of the structure at the nanoscale on the functionality of the systems, I will demonstrate that even inorganic systems are alive and dynamic under reaction conditions.

COLL 118

Puzzling electrical conduction in ionic surface channels fabricated by interfacial electron beam chemical patterning of highly ordered n-alkylsilane monolayers on silicon - a synthetic single-layer material

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Interfacial electron beam lithography (IEBL) is a novel chemical patterning methodology that enables nondestructive local functionalization of the outer surfaces of highly ordered n-alkylsilane monolayers on silicon via chemical conversion of their top -CH₃ groups to -COOH while fully preserving the overall molecular organization and structural homogeneity of the monolayer. IEBL-fabricated single-layer channels consisting of ionizable -COOH surface paths with precisely defined micrometer-to-centimeter lengths and widths down to less than 20 nanometers exhibit unusual lateral electrical conduction, critically dependent on their dimensions, the nature of the metal electrodes contacting the channel, the type and conductivity of the underlying silicon substrate, the proximity of the channel to the silicon surface, the nature of the insulating spacer between the channel and the silicon surface, and the presence and nature of a top cover layer. The interplay between these different system parameters allows modulating the conductivity of a given channel between that of a practical insulator to some abnormally high values. Empirical correlations based on a comprehensive characterization methodology that combines electrical measurements with multi-mode AFM imaging, quantitative FTIR and micro-FTIR measurements, and post-patterning chemical derivatization and nanoscale self-assembly capabilities point to a complex conduction mechanism that involves coupled ionic-electronic transport mediated and enhanced by interfacial electrical interactions with charges locate outside and separated from the channel carrying the measured current. These unprecedented findings may not be rationalized on the basis of known charge transport mechanisms.
From colloidal synthesis to integration: Hybrid materials for infrared nanophotonics

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We describe the synthesis, optical characterization and integration of suppressed-blinking, photostable infrared quantum dots (QDs). For example, we successfully “engineered” the shell and core/shell interface of InP/CdSe quantum dots (QDs) to exhibit blinking-suppressed two-color (infrared and visible) excitonic emission. A “giant” (thick) shell enabled strong shell-dependent blinking suppression of the infrared emission that is characteristic of this type-II QD system. On the other hand, synthetic “engineering” of defect states at the core/shell-interface afforded an unexpected two-color emission, as visible emission from the shell could be controllably turned on or off by choice of reaction chemistry. In the case of lead salt gQDs, we show for the first time that photoluminescence is stable—non-blinking and non-photobleaching—without polymer or glass encapsulation to telecom O and S bands. The advances in control over colloidal shell-growth processes that enabled this new behavior will be described. Lastly, the enhanced stability afforded by optimizing synthesis for a targeted functionality allows nanoparticle integration into photonic structures, such as optical nanoantenna and nanoscale resonators. An approach using a scanning probe nanolithography technique to prepare new hybrid emitter-antenna infrared materials will be shown.

Colloidal CdSe 0-dimension nanocrystals and their self-assembled 2-dimension structures

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An extraordinary type of CdSe semiconductor nanocrystals (NCs) that exhibit a single optical absorption doublet has generated a lot of interest. The peak positions of the doublet vary with passivation ligands (at ~426 nm and ~453 nm for amine ligand passivation and at ~432 nm and ~460 nm for carboxylate ligand passivation). The peaks are relatively sharp with 10 nm full width half maximum. To date, it has been generally concluded that these NCs have a two-dimension (2D) morphology with 1D quantum confinement. Here, we demonstrate that zero-dimension (0D) NCs with 3D quantum confinement can exhibit a very similar static optical feature. This 0D morphology could result in the appearance of 2D NCs via post-treatment. Our findings indicate that a well-like morphology can be induced by the presence of a primary amine, hexadecylamine (HDA), in the dispersion with sonication for amine-passivated 0D NCs or by the use of ethanol during purification with dispersion storage for carboxylate-
passivated 0D NCs. Our study calls for efforts on sophisticated theoretical studies for
the experimental observations.

**COLL 121**

**Colloidal superparticles from crystallization of artificial atoms**

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Colloidal superparticles are collections of nanoparticles (or artificial atoms) in the form of
colloidal particles. Assembling nanoscopic objects into meso/macroscopic complex
architectures allows bottom-up fabrication of functional materials, which is essential for
many nanomaterial-based technological applications. In this talk, we shall discuss the
science on the nucleation and growth of colloidal superparticles with supercrystalline
structures made from the self-assembly of nanoparticles in closed thermodynamic
systems. We shall show that the enthalpic and entropic factors of closed
thermodynamic systems are controllable by the choice of nanoparticle’s composition,
size and shape, nanoparticle ligands and their configurations, and superparticle
surfactants and solvents. The interplay between these enthalpic and entropic factors
mediates the self-assembly of nanospheres, nanorods, and nanocubes, leading to the
formation of mesoscopic colloidal superparticles exhibiting well-defined magic-sized
superclusters, multiple well-defined supercrystalline domains, and binary superlattice
structures. Further, we shall show that colloidal superparticles are important building
blocks for creating new types of functional materials. For example, superparticle solids,
with high-pressure treatments, can form metastable crystalline phases at ambient
pressure and temperature.

**COLL 122**

**Looking at lead salt nanocrystals one by one at low temperature and under high
magnetic field**

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Low temperature single quantum dot photoluminescence spectroscopy has been an
indispensable tool in probing the intricate details of the band edge excitonic states such
as their homogeneous linewidths and phonon assisted transitions. Adding high
magnetic field and polarization resolving capabilities further strengthen this experiment
toward probing not only the symmetry of transition dipole and fine structure splitting
resulted from shape anisotropy but also spin-degeneracy lifting and the optically
forbidden transitions brightened by the magnetic field. While II-VI and III-V nanocrystals
have been investigated extensively using these powerful single dot experiments, only a
few room temperature experiments mainly focusing on blinking properties of single lead
salt nanocrystals has so far been reported. Thus, intrinsic properties of band-edge excitons starting from homogeneous linewidths of lowest emissive state to nature of transition dipole remains poorly understood. Here we report the first comprehensive, polarization resolved, PL study for individual PbS/CdS core/(thick Shell) QDs conducted over 4 -300 K temperature range and under high magnetic field up to 8.5 T. Our experiment revealed (1) 8- 24 meV intrinsic linewidth reflecting ultra-fast dephasing, (2) broad low energy sideband attributable to phonon assisted transitions of LO phonons at X and Γ points, (3) evidence of 3D transition dipole, (4) Zeeman splitting and g factor and (5) anisotropic exchange splitting arise from shape asymmetry of the QD core.

COLL 123

Orientational order in self-assembled nanocrystal superlattices

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Self-assembly of nanocrystals into functional materials requires precise control over nanoparticle interactions in solution, which are dominated by organic ligands that densely cover the surface of nanocrystals. In this talk, I will present a computational study of ligand effects in the self-assembly of small, non-spherical nanocrystals. We focus on nanocrystals with cuboctahedral and truncated octahedral shape and determine their self-assembly behavior as a function of ligand length and solvent quality. Our model, which is based on a coarse-grained description of ligands and a schematic representation of solvent effects, reproduces the experimentally observed superstructures, including recently observed superlattices with partial and short-ranged orientational alignment of nanocrystals. We show that small differences in nanoparticle shape, ligand length and coverage, and solvent conditions, can lead to markedly different self-assembled superstructures due to subtle changes in the free energetics of ligand interactions. Our results help explain the large variety of different reported superlattices self-assembled from seemingly similar particles and can serve as a guide for the targeted self-assembly of nanocrystal superstructures.

COLL 124

Aptamer-based rapid whole cell detection and quantification of pathogens

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Infectious outbreaks caused by pathogenic bacteria are still occurring worldwide and cause acute illnesses and significant industrial impact. In this work, for the first time, we demonstrated a platform that uses aptameric DNA sequences, covalently conjugated to a 4-Aminothiophenol-Gold nanoparticles complex, for the sensitive and highly specific detection of pathogenic bacteria. Low concentrations of E. coli O157:H7 were detected (~10^2 CFU/mL) within 15 minutes in both pure culture and ground beef samples. A
strong linear correlation between Raman signal intensity with increasing concentrations of *bacteria* (10² to 10⁶ CFU/mL) ($r^2=0.995$) was demonstrated. Specificity was tested vs. *Listeria monocytogenes* (10⁶ CFU/mL), demonstrating that there is not a significant difference ($p = 0.786$) between the control samples and the interferent bacteria cells. This approach may potentially be applied simultaneously to different pathogenic bacteria in a multiplexed fashion employing unique Raman probes and strain-specific aptamer sequences.

**COLL 125**

**Safe-by-design hybrid nanoparticles of antimicrobial silver, aminocellulose, and quorum quenching acylase eradicate bacteria and their biofilms**

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The emergence of drug resistant bacteria and the failure of the existing therapeutics call for development novel antibacterial strategies. Furthermore, the inclusion of pathogens in highly organized biofilms restricts the drug penetration and efficiency, causing life-threatening infections and lead to poor treatment outcomes. The process of biofilm formation is controlled by the phenomenon of cell-to-cell communication, known as quorum sensing (QS). Targeting the QS system of the pathogens is an emerging area of research relying on the capability of the anti-QS agents to attenuate bacterial virulence and biofilm formation, making the cells more susceptible to the conventional drugs at lower concentrations. Interfering with bacterial QS may potentiate the efficacy of current antimicrobials and lower the risk of resistance development. Herein, we developed innovative nanosized hybrid entities of silver nanoparticles (AgNPs) decorated with layers of bactericidal aminocellulose (AC) and anti-infective/antibiofilm enzyme acylase in a Layer-by-Layer (LbL) fashion. The AC and acylase nanoshell targeted the functions essential for bacterial pathogenesis and enhanced the antibacterial activity of the AgNPs towards Gram-negative *Pseudomonas aeruginosa* (*P. aeruginosa*), lowering their minimum inhibitory concentration by 4-fold. These nano-sized hybrid entities interfered with the QS regulated virulence factors production by 45 % and were able to inhibit and eliminate *P. aeruginosa* biofilms at 8-folds lower concentration of AgNPs template. The side effect of AgNPs to human cells was decreased upon decoration with AC and acylase and at determined effective bacteria eliminating concentrations our hybrid NPs did not affect the cells morphology and viability. This in turn make these hybrid NPs with multiple targets for killing mechanisms promising alternative to manage difficult-to-treat bacterial pathogens, exerting less selective pressure for resistance occurrence.

**COLL 126**

**Understanding the dynamics of phospholipid membranes using field cycling NMR**
We study membrane dynamics of phospholipid liposomes in aqueous solutions using Fast Field Cycling (FFC) \(^1\)H NMR and Field Cycling (FC) \(^{31}\)P NMR. Proton Fast Field Cycling NMR allows us to investigate dynamics over a wide time range spanning from translational diffusion to order fluctuations to individual lipid rotations. We investigate the differences in dynamic processes occurring with changes in environmental conditions. Further, we employ \(^{31}\)P Field Cycling NMR technique which will help understand unique dynamics in the zwitterionic phosphatidylcholine head group. The sensitivity to headgroup motions allows us to simplify the dynamics and obtain a better understanding of the surface dynamics of the bilayer. Finally, we combine the investigated dynamics with the results obtained by Neutron Spin Echo (NSE) in order to obtain a broader picture of the dynamics occurring in phospholipid liposomes and their uniqueness in serving as a model for understanding cell membrane dynamics.

**COLL 127**

**Light triggered, cell-specific liposome fusion and drug delivery in vivo**

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In this work, we describe an effective and versatile strategy to ‘turn on’ the targeting of nanomedicines to specific cells in vivo and on demand. At the heart of this approach is the use of light to trigger the de-shielding of nanomedicine surfaces to reveal underlying functionality. Here, light triggered activation of intravenously injected and freely-circulating liposomes resulted in the rapid and specific targeting of cancer cells within a xenograft zebrafish embryo model. Crucially, no liposome interactions with any other cell type (including macrophages and scavenging endothelial cells) was observed prior to or following light activation. Furthermore, in this case, liposome binding to target cancer cells led to direct liposome-cell fusion and concomitant drug delivery direct to the cell cytosol (as opposed to endocytotic liposome uptake). This resulted in significantly enhanced efficacy as compared to treatment with free drug alone.

**COLL 128**

**Functional biomembranes entrapped within mesoporous silica and titania gels**

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Entrapment of biomembranes in mesoporous metal oxide gels has proven to be a challenge, as current and previous techniques utilize liposomes as biological membrane hosts. The instability of liposomes in mesoporous gels is attributed to their size and altered structure and lipid dynamics upon entrapment within the nanometer scale pores (5-50 nm) of silica gel. We have overcome these barriers by using nanolipoprotein particles (NLPs) as biomembrane hosts. NLPs are discoidal patches of lipid bilayer that are belted by amphiphilic scaffold proteins and have an average thickness of 5 nm, with diameters ranging from 10-15 nm. To ensure proper functioning of gel-entrapped NLPs, we have investigated the phase behavior of the lipids in addition to the secondary structure, localization, and environmental polarity of the scaffold proteins. Our results indicate that gel-entrapped NLPs remain intact, with only slightly altered lipid and scaffold protein structure and dynamics. In addition, the integral membrane protein bacteriorhodopsin (BR) in its native purple membrane has been successfully encapsulated within titania gels as evidenced by substantial retention of the characteristic visible spectral absorbance over 20 days and pink-purple color. This was accomplished through our development of sol-gel processing conditions to eliminate the use of organic solvent after demonstrating that inclusion of organic solvents eliminated the characteristic BR visible spectra. Once encapsulated in the wet gel, BR was shown to reversibly convert from its dark adapted (mixed 13-cis- and all-trans-retinal cofactor) to its light-adapted (all-trans-retinal) state, and to retain its thermochromic behavior, indicating that the pores did not hinder the membrane protein’s functionality to make conformational changes in response to its environment. This suggests that BR, whether in purple membrane or in a membrane nanodisc, will retain its ability to function as a proton pump, a factor in favor of using the protein over a conventional dye for sensitizing mesoporous titania gel to permit visible light photocatalysis and photocurrent generation. Moreover, we showed that the titania gels display the characteristic titania band-gap of 3.4 eV and were photocatalytic at a level comparable with commercial crystalline nanopowders under UV irradiation. In addition to these results, our most recent progress will be presented.

COLL 129

Functionalized lipid carriers for nucleic-acid and drug therapeutics

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Liposomes are the most widely studied synthetic carriers worldwide for nucleic acid (NA) and drug delivery applications. Cationic liposomes (CLs) are relatively safe vectors used in ongoing clinical trials. The talk will first describe experiments with surface-functionalized PEGylated CL–DNA nanoparticles (NPs), including fluorescence microscopy colocalization with members of the Rab GTPases, which has revealed NP pathways and interactions with cells. The functionalization, achieved through custom
synthesis, is intended to address and overcome cell targeting and endosomal escape barriers to delivery faced by NPs designed for in vivo applications. We will further discuss recent results with CL-paclitaxel (PTXL) NPs involving a mechanistic understanding of the relation between structure and physicochemical properties of CL-PTXL NPs and PTXL delivery efficacy leading to cytotoxicity against human cancer cells.

**COLL 130**

**Stressful process of patterning fluid-solid membrane domains**

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Phase separation of multicomponent phospholipid membranes can, for different membrane compositions, lead to fluid-fluid or fluid-solid coexistence of microscopic and nanoscopic domains. The solid domains are thought to be comprised, typically, of a gel phase in which molecules are tilted relative to the membrane surface; however, saturated-tail phosphatidylcholine lipids also have produced solids with ripple or corrugated structures, at least in single-lipid systems. Using different tracer lipids we have demonstrated polymorphism in the patchy or striped solid membrane domains formed during the cooling of giant unilamellar multicomponent vesicles. Observations are currently best explained by the formation of the gel at elevated tensions or, at long times low temperatures. Low tensions permit the formation of compact ripple phase domains. We show here how the formation of patches versus striped domains can be difficult to anticipate and therefore challenging to control because of the complex interplay between cooling rate, osmolarity, and membrane compositions, all variables that alter the vesicle tension as domains are forming. We additionally explore the interplay between membrane tension and rigid vs fluctuating curvature to produce long range ordering of patchy domains, controlling whether the domains are limited by vesicle curvature and whether they arrange into strings of patches or assemble with uniform spacings.

**COLL 131**

**Lateral organization in live cells and model biomembranes**

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The existence and role of lateral lipid organization in biological membranes has been studied and contested for more than 30 years. Lipid domains, or rafts, are hypothesized as scalable compartments in biological membranes, providing appropriate physical environments to their resident membrane proteins. This implies that lateral lipid organization is associated with a range of biological functions, such as protein co-localization, membrane trafficking, and cell signaling, to name just a few. I will discuss
recent work using neutron scattering to probe the structure and mechanical properties of lipid bilayers in both model lipid systems and in living cells. These experiments have provided direct observations of cell membrane transverse and lateral structure, showing the average hydrophobic thickness of the *Bacillus subtilis* cell membrane and evidence of ~ 40nm lipid rafts based on laterally heterogeneous fatty acid distribution. Ongoing work continues to leverage neutron scattering methods model bilayers, examining differences between distinct lipid phases in terms of structure, mechanical properties, and lateral diffusion rates. Observing such differences in models allows us to feedback iteratively into models of phase separation/lateral organization in living cells.

**COLL 132**

**Phase-forming mechanism in multicomponent lipid mixtures**

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Biological membranes exhibit a great deal of compositional and phase heterogeneity due to hundreds of chemically distinct components that form the membrane. Its phase behaviour is enormously complex and therefore the study of the phase separation processes using a cell membrane is extremely difficult. Even the phase behaviours of simple binary or ternary model membranes are remarkably rich, however we still lack the fundamental understanding of the formation of domains of different sizes in multicomponent systems. In the present work, we hypothesize that the phase separation in multicomponent mixtures on macro scale is governed by the formation of coupled nanometer-sized lipid “pairs”. The lipid concentration- and temperature-dependent nucleation of such stable entities leads to different phases on a phase diagram. Using inelastic x-ray scattering we provide the direct experimental evidence for the stable lipid “pairs” through observation of optical phononic modes in binary (DPPC-Cholesterol) and ternary (DPPC-DOPC/POPC-Cholesterol) systems.

**COLL 133**

**Undulated films of conformationally asymmetric binary lipids and polymer blends**

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Abundance of curved structures and rich variety of shapes within cells steer us to the idea that curvature is linked with cellular functions. In fact, there is an agreement that chemical composition in membranes and their local curvature is coupled, and this could provide avenues of mechanically controlling the spatial organization of membrane components, such as proteins and other lipids. To quantify mechnochemical couplings in membranes, supported lipid membranes on corrugated substrates have been used as model systems, in which fabricated surfaces impose specific curvature patterns onto mixed lipid bilayers. In order to study connections between bending rigidities of the
lips and chemical composition in spatially non-uniform membranes, we use coarse-grained molecular dynamics simulations and self-consistent field theory (SCFT) to simulate lipids and binary polymer blends, respectively, confined between sinusoidal surfaces. Decisive role of the conformational asymmetry between the two components, either lipids or polymers, in inducing domain formation and sorting on corrugated surfaces will be discussed. Qualitative comparisons with phenomenological models presented in the literature for the formation of lipid rafts will be presented.

Conformationally asymmetric polymer blends confined between sinusoidal surfaces of different curvatures characterized by amplitude (a) and wavelength (\( \lambda \)).

**COLL 134**

**High-index facet particle shape regulation by dealloying**

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Nanostructures with high-index facets are extremely important in catalysis, yet limited ways for producing them in ligand-free form at scale exist. Typically, either relatively low throughput electrochemical methods or higher throughput solution-phase methods that rely on facet-stabilizing ligands are used to prepare them. Importantly, the atomic structure of such facets can directly influence catalytic activity. However, the use of ligands to control particle shape is limiting for two reasons. First, the role of such agents is not well understood, and different ligands are required, depending on metal type and desired particle shape. Second, stabilizing ligands are often difficult to remove and adversely affect catalytic activity by blocking active sites. Therefore, a significant advance would be the development of a straightforward, ligand-free, and generalizable
method for making nanoparticles with high-index facets. Here, we demonstrate that high-index facet Pt, Pd, Rh, Ni, Co, and a library of bimetallic tetrahedra (THH) can be synthesized by a ligand-free, solid-state reaction that employs trace Sb, Bi, Pb, or Te elements as high-index facet stabilizing agents. Both density functional theory (DFT) calculations and experimental results confirm the role of these trace elements with respect to stabilizing the {210} planes of the resulting THH. A study of the PtSb system shows that the THH shape results from the evaporative removal of Sb from the initial alloy, a shape-regulating process that is fundamentally different from solution-phase, ligand-dependent, additive-growth processes. Remarkably, THH particles form regardless of the initial shape of the particles, making this strategy attractive for recycling waste catalysts that are not in industrially useful forms. Finally, the Pt-based THH were evaluated as electrocatalysts for formic acid oxidation and determined to be superior to commercial Pt/C catalyst, thereby providing a promising alternative that may become important in next-generation fuel cell development.

COLL 135

Controlling the surface of dilute bimetallic nanoparticles via halide-mediated metal ion reduction

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Achieving selectivity in challenging catalytic transformations requires fine control over catalyst surface structure and composition. Shaped nanoparticles with well-defined facets and dilute bimetallic surface compositions provide a broad range of tunable surface reactivity. However, generating nanoparticles with specific desired surface structures and compositions in bimetallic systems presents additional synthetic challenges relative to monometallic materials, including significant differences in metal precursor reduction potentials. We show that low-micromolar concentrations of halide ions can be used as a tool to differentially tune the relative rates of reduction of two metal precursors in a co-reduction system to yield shaped nanoparticles with dilute bimetallic surface compositions and well-defined but undercoordinated surfaces. This approach is applicable to the production of materials with a range of surface compositions, including (Pd)Au, (Cu)Pd and (Ag)Au, with the minority metal indicated by parentheses. We will also discuss alternative methods for the synthesis of dilute bimetallic materials with controlled surface facets, such as a post-synthetic underpotential deposition approach, as well as the emergent catalytic behavior of these materials for selective oxidation and selective hydrogenation reactions.

COLL 136

Engineering of colloidal nanocrystals for multifunctional coatings

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While progress in physical deposition techniques, such as sputtering and CVD, has allowed thin film deposition techniques to generally keep pace with the performance requirements of typical optical and semiconductor applications, this performance comes at a significant cost, impacting budget, logistics, and environmental, safety, and health areas. Development of solution processing methods for the synthesis of functional inorganic materials have opened up new avenues to achieve enhanced and/or novel properties in these materials. Among significant methods, self-assembly techniques are one of the powerful, efficient, and cost effective methods to the synthesis of nanostructured films. Using these techniques and their combination with top-down fabrication processes such as lithography, materials with hierarchical feature can be produced with form and function in multiple length scales. Here our recent progress in development of engineered multifunctional nanostructured coatings using self-assembly techniques will be presented. An interfacial self-assembly process is developed to synthesize multifunctional colloidal nanocrystals and to assemble them into ordered, three-dimensional, nanoparticle films. Through control of structural parameters of nanocrystal assemblies, we are able to fabricate uniform reflective optical coatings. Quarter wave stacking of self-assembled nanocrystal films are developed for near infrared reflectors, which overcomes the harsh conditions from conventional processing (CVD, sputtering, etc) with improved functionality. Reflectivity studies show high and reproducible reflectivity over controlled wavelength windows (1-12µm). Theory modeling shows very good consistency with experimental results.

**COLL 137**

**Chemical potential of metal atoms in supported and unsupported nanoparticles: Dependence upon particle size and support**

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Metal nanoparticles supported on oxide surfaces form the basis for many industrial catalysts and promise to play an ever increasing role in future energy and environmental technologies. The chemical potential ($\mu$) of the metal atoms in these particles depends strongly on particle size and support, and is an important factor that determines their catalytic properties, including their binding strengths to adsorbed reaction intermediates and their long-term stability against sintering. We have measured this chemical potential for many later transition metal on oxide supports and showed that is well approximated for particles of effective diameter $D$ by

$$\mu(D) = [(3\gamma_m - E_{adh})(1 + D_0/D)](2V_m / D),$$

where $\gamma_m$ is the surface energy of the bulk metal, $E_{adh}$ is the adhesion energy at the bulk metal / oxide interface, and $D_0$ is $\sim 1.5$ nm, and $V_m$ is the molar volume of the bulk metal. This contrasts with the Gibbs-Thompson Relation for unsupported spherical nanoparticles:

$$\mu(D) = 4\gamma_m (2V_m / D),$$

which has no contribution from adhesion energy. Based on the above results, we argue...
that this should be revised to:
$$\mu(D) = 4\gamma_m (1 + D_0/D)(2V_m / D),$$
with the same $D_0$ value for metal nanoparticles. This is crucial for understanding particle stability and growth kinetics during synthesis. Methods to estimate $\mu(D)$ in core-shell nanoparticles will also be discussed.
To estimate chemical potential versus particle size for oxide-supported metal supported particles, one only needs to know $E_{adh}$, since $\gamma_m$ is well known, at least for pure metals. We further show that $E_{adh}$ increases with: (1) increasing heat of formation of the most stable oxide of the metal from metal gas atoms plus $O_2(gas)$ per mole of metal atoms, and (2) increasing density of surface oxygen atoms on the oxide surface.

**COLL 138**

**Spectral-selective plasmonic polymer nanocomposites**

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The state-of-the-art commercial tinted glass is coated with a full layer of metalized film to decrease the transmittance of electromagnetic waves. In addition to the cost of the metal layer, the key limitation of such light-reflecting glass is the lack of spectral selectivity. To date, there has been no demonstration of stable and spectral-selective glass that covers the entire visible and near-infrared (NIR) spectrum. To address the challenge, herein by judiciously controlling the planar orientation of 2D plasmonic silver nanoplates (AgNPs) in polymer nanocomposites, we effectively harness the transmittance, reflectance, and filtration of any wavelength across the visible and NIR. In contrast to the conventional bulk polymer nanocomposites where plasmonic nanoparticles are randomly mixed within the polymers, our thin-film polymer nanocomposites employ a minimal amount of planarly oriented metal nanoparticles and yet efficiently manage light across the visible and NIR. The thin-film polymer nanocomposites are expected to impact enormously on spectral-selective tinted glass, as well as on sensing, optics, optoelectronics, and photonics.

**COLL 139**

**Preparation and characterization of a new erlotinib polymorph**

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Changes in the three-dimensional spatial arrangements of pharmaceutical compounds, known as polymorphisms, can drastically change a drugs’ physical characteristics and chemical interactions within the human body. Polymorphism in pharmaceuticals is one of the most important aspects in the drug development and distribution processes. When a polymorphism arises, it can cause changes in bioavailability, toxicity, and
stability. Consequently, these are the reasons that make the characterization of polymorphs vastly important. In this study Erlotinib, commercially marketed as Tarceva®, is of interest as it is relatively new and not been substantially researched in order to discover new polymorphs. Erlotinib is used in the treatment of non-small cell lung and pancreatic cancers, and the discovery of any potential polymorphs could indicate the potential to enhance its treatment. Erlotinib underwent heterogeneous nucleation by using phosphonate self-assembled monolayers attached to zinc oxide tiles. In addition, sublimation and melting techniques were used in attempt to isolate single crystals of possible new polymorphs. To characterize the potential polymorphs, multiple techniques were utilized, including: infrared spectroscopy, Raman spectroscopy, powder X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscope, and solid-state nuclear magnetic resonance. All of these characterizations have led to the conclusion that a new polymorphic form of Erlotinib was created.

COLL 140

Manipulation of gold nanostructures for imaging applications using a single-beam optical trap

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Optical traps have applications in various disciplines of science specifically biology (cells) and physics (statistical physics). The goal of this project is to measure the force constants of gold nanoparticles of various sizes utilizing the equipartition and power spectral density method with enhancement of force constants through plasmonic resonance of gold nanobars. The current gold nanoparticles being analyzed lie in 40-60 nm range, however larger and smaller particles can be trapped. Synthesized particles are trapped using a 1064 nm laser in combination with a high numerical aperture resulting in a tight focus of the beam. Experiments involve modifying the setup of the optical table to include a galvo scanning mirror to measure force constants. Potential benefits of this research are to allow for the isolation of single particles to perform single particle optical spectroscopy on both organic and inorganic nanostructures. Isolation of single particles allows for the analysis of a particle to see individual behaviors of various sizes in a solution. Results from measuring the force constant of the trap will be presented.

COLL 141

Modification of Inorganic Oxides with Poly(hydridomethyl)siloxanes as an Approach to Mixed Functional Surfaces
Over the last several years, reactions between siloxane polymers or monomers with inorganic oxide surfaces have become more prominent, owing to the increasing acceptance of the siloxane bond as a functional, reactive group. However, while these reagents create excellent low hysteresis surfaces, they do not provide for further functionalization. Poly(hydridomethylsiloxane)s (PHMS), on the other hand, react readily with a wide variety of inorganic oxide surfaces while providing a scaffold for subsequent functionalization. Herein, we discuss the preparation of PHMS-modified silica surfaces. Reaction conditions show a significant influence on the resulting surface, with temperature dependence on the dominant reaction mechanism. These PHMS surfaces also exhibit low contact angle hysteresis, but can be further modified through cross-coupling reactions, such as hydrosilylation, to create more advanced monolayers. Surfaces are examined via dynamic contact angles, ellipsometry, and x-ray photoelectron spectroscopy (XPS) to show changes in the surface chemistry with subsequent modifications, and their effects on wettability.

**COLL 142**

Solution-based green amplified spontaneous emission from colloidal perovskite nanocrystals exhibiting high stability

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Solution-based optical amplification, compared to solid-state thin-filmed based optical amplification, affords a plethora of benefits ranging from versatility in gain medium dimensions to stability afforded by improved heat dissipation. Works reporting solution-based optical amplification, however, remain sparse due to the difficulty in achieving high volume fractions required for optical amplification in liquid mediums. In this work, we demonstrate highly stable amplified spontaneous emission (ASE) from a solution of green-emitting CsPbBr₃ perovskite nanocrystals dispersed in a non-polar solvent after a facile post-synthesis process. This process not only allows for the purification of nanocrystals, but also retains the surface ligand density required for high volume fractions. Photostability tests also show sustained ASE intensities in excess of three hours under high, continuous photoexcitation of femtosecond pulsed laser beam far exceeding those of thin films by an order of magnitude. This work demonstrates for the first time green liquid ASE through CsPbBr₃ nanocrystals that is both versatile in containment and in applications which could aid in the development of dynamically tunable full-visible spectrum optical amplification for fluidic optical sensors and stable white ASE.

**COLL 143**
Graphene oxide-metal hybrid systems for sensing and catalysis

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Graphene oxide (GO) serves as a precursor to various technologies, which include batteries, biosensors, solar cells, and supercapacitors. Metal hybrids of GOx enhance the sensitivity and electrical conductivity for sensing and catalytic applications. In this project we use silver and palladium nanoparticles independently to modify the surface of GOx. Silver nanoparticles exhibit optical properties that play a role in bacterial resistance, demonstrating its role in various biomedical sensors. Palladium nanoparticles are highly sensitive and functional in room temperature; making it an ideal metal for catalytic applications. Here we report the synthesis of functional graphene oxide from graphite flakes, followed by both successful carboxylation and reduction. In this experiment, carboxylation of GOx was followed by insertion of silver nanoparticles through an oleylamine ligand. Reduction of GOx resulted in a highly conductive, monolayer graphene quantum dot, which will be coated with palladium nanoparticles and utilized in catalytic applications, primarily Suzuki cross-coupling reactions. The Pd-GOx will serve as a cheaper and stable alternative as compared to traditional palladium-based catalysts used in these reactions. Initial results of our experiment will be presented.

COLL 144

Synthesis and characterization of a conductive biomimetic hydrogel nanocomposite for responsive wound management technologies

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Hydrogel nanocomposites have become the focus of much research in the wound management field due to their swelling properties, tensile strength, and ability to act as a scaffold for cell growth. As wounds secrete, the exudate diffuses into the hydrogel resulting in a wet environment that can propagate skin cell growth while decreasing the chance of infection. Additionally, the nanocomposites can be modified with active components, such as a conductive layer, to elicit a response upon changes in the surrounding environment. This research focuses on the synthesis and characterization of a responsive hydrogel nanocomposite that upon external stimulus enhances its conductive properties and ultimately produces a signal. The synthesized nanocomposite is comprised of a biomimetic, alginate-based hydrogel layer and a cellulose-polyaniline (PANI) conductive layer which acts as the active component by generating a signal upon swelling. As ions diffuse through the alginate layer into the PANI layer, electrons transfer more readily thereby increasing the conductivity of the nanocomposite resulting in a signal via an LED. This signal can be correlated directly with the degree of swell of the hydrogel and therefore indicate when the gel has reached maximum swell capacity.
Initial results have shown that after 150 minutes on a simulated wound surface, the hydrogel swells over 150% and increases the lux efficiency of an LED by 20%.

**COLL 145**

**pH-Responsive nanoparticle embedded catalysts for imaging of biofilm-associated infections**

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Multi-drug resistant bacterial infections are responsible for 700,000 deaths each year worldwide, with more than 10 million deaths per year predicted by the year 2050. The majority of human bacterial infections (~80%) are associated with formation of biofilms on living-tissues. Early detection of biofilms is crucial for limiting infection-based damage. Imaging these biofilms is challenging: conventional imaging agents are unable to penetrate the dense matrix of the biofilm, and many are susceptible to false positive/negative responses due to phenotypical mutations of the constituent microbes. We have engineered nanomaterials to penetrate the extracellular polymeric substance (EPS) matrix of biofilms and to intrinsically target the acidic microenvironment of the biofilms. Here, we report the creation of pH-responsive nanoparticles with embedded transition metal catalysts (nanozymes) that effectively target the acidic microenvironment of biofilms. These pH-switchable nanozymes generate imaging agents through bioorthogonal activation of profluorophores inside biofilms. The specificity of these nanozymes for imaging biofilms in complex biosystems was demonstrated using biofilm-mammalian cell co-culture experiments.

**COLL 146**

**Sum frequency generation imaging microscopy of self-assembled monolayers on metal surfaces: Factor analysis of multicomponent mix monolayers**

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Surfaces and interfaces are considered as a boundary between a material and its surrounding environment and influence interactions with that environment. In order to gain a fundamental understanding of the underlying processes it is critically important to know the chemical and physical properties of the surfaces or interfaces. To investigate surface properties, while controlling the surface chemically and spatially, a model system of patterned self-assembled monolayers (SAMs) with different terminal functional groups was produced by microcontact printing. The microcontact patterned
self-assembled alkanethiol monolayers on gold surfaces were analyzed by sum frequency generation imaging microscopy (SFG-IM) technique to generate SFG images. The SFG-IM provides identity of surface/interface molecular species, information about surface/interface chemical structure, and spatial distribution overview of chemicals on the surface, which make it a useful technique in chemical imaging. The SFG images were then analyzed by factor analysis (FA) to determine the spatial distribution of the patterned monolayers over the images. Factor analysis is a statistical method that uses mathematical procedures to investigate whether a number of observed variables are linearly related to some smaller number of unobservable factors. Additionally, each significant abstract factor produced by FA was assessed to determine the information contained within the abstract factor. These results indicate that FA of the SFG spectra is a promising method to determine the composition and identities of mixed alkanethiol systems that consist of different terminal functional groups. Factor analysis has also successfully been applied to SFG images obtained with low signals to extract individual species spectral information.

COLL 147

Preparation of sol-gel GeO$_2$ and GeO$_2$-SiO$_2$ nanoparticles for use in 3D printed optics

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Additive manufacturing, or 3D printing, is particularly attractive for the fabrication of flat freeform optics. These differ from conventional optics in that they do not rely on the geometry of the lens to guide light. Instead, flat freeform optics exploit a change in refractive index by spatially varying the percent of dopant, in this case GeO$_2$. The ability to conveniently fabricate flat-refractive index graded optics would be paradigm shifting, allowing for more compact optical design and reduced wavefront loss. In this presentation, we report the preparation of sol-gel derived GeO$_2$-SiO$_2$ core-shell particles that can be formulated into an ink for use in direct ink write 3D printing glass optics. Results discussed will include efforts to prepare GeO$_2$ core and GeO$_2$-SiO$_2$ core-shell particles which have are both small (sub-100 nm in diameter) and colloidally stable. The role of varying the ratio of water, catalyst, and solvent to the GeO$_2$ precursor, as well as the reaction temperature will be discussed. For glass production, we show the preparation of transparent and semi-transparent glasses over the range of 5 to 25 wt% GeO$_2$ dopant. Ongoing studies include the chemical characterization of the core and core-shell particles at various stages of particle growth and glass formation.

COLL 148

Biomimetic, peptide-directed synthesis of size-controlled iron oxide nanoparticles
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Peptides and proteins are widely used in nature to direct the growth of various inorganic structures including bones and shells, as well as nanoparticles of controlled geometry, in a process called biomineralization. Of particular interest, many organisms use the globular protein ferritin for iron storage by coordinating the growth of iron oxide nanoparticles and constraining their size to a narrow distribution. This study aims to reproduce this process of controlled nanoparticle growth using a much simpler, engineered peptide. This peptide is incorporated into polyelectrolyte complex micelles, allowing for solubilization of the nanoparticles and preventing their aggregation. These nanoparticle-containing micelles could in turn have applications for nanodevices, due to the magnetic properties and controlled geometry of the nanoparticles.

COLL 149

Synthesis, modification, and integrity of zinc oxide nanoparticles for RNA delivery

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Nanoparticles are becoming ubiquitous delivery systems in the biomedical sciences and can be layered with different compounds to produce vessels for transportation of biological materials. In particular, gold nanoparticles have successfully been utilized for the delivery of biological materials into cells. However, gold nanoparticles are synthesized from expensive precursors. Herein, we demonstrate that zinc oxide nanoparticles are more affordable alternatives for the delivery process. Zinc oxide nanoparticle conjugates were synthesized, modified and utilized for the delivery of proteins and ribonucleic acids. The zinc oxide nanoparticle conjugates were characterized with Dynamic Light Scattering Spectroscopy (particle sizing), Scanning Electron Microscopy (particle size and morphology), Electrophoretic Mobility (surface charge) and UV-Vis Spectrophotometry (optical properties). Preliminary results indicate that the biological activity of the proteins and ribonucleic acids was maintained and, in some cases, even better compared to other nanoconjugates.

COLL 150

Development of pH-responsive microgels for nanoparticle-based detection methodologies

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In this study, pH-responsive microgel particles, comprised of 2-vinyl pyridine (P2VP) and styrene, are explored as scaffolds to assemble metallic and semiconductor nanoparticles (NPs) for ultrasensitive detection strategies. In the first case, microgel particles serve as size-tunable scaffolds to assemble metal (silver or gold) NPs for surface-enhanced Raman scattering (SERS). The high sensitivity of SERS arises from the enormous enhancement of the Raman scattering cross sections of molecules adsorbed to roughened metal surfaces, such as metal NPs. Using a sterically stabilized latex of random copolymers of polystyrene and P2VP, this polymer is capable of transitioning to a microgel state through acid-base titration. This effect can manipulate the interparticle spacing between adsorbed metal NPs in order to optimize SERS enhancement. These microgel-NP composites are characterized and their pH-responsive behavior is demonstrated to be reversible. In a second approach, the ability of the P2VP-styrene microgel system to encapsulate luminescent semiconductor quantum dots (QDs) is examined. Aggregation of hydrophobic QDs is controlled by embedding them in hydrophobic P2VP and styrene monomeric micelles before initiating cross-linking in an aqueous solution. By controlling the monomer to QD ratio, the number of QDs embedded in the resulting microgel particles is controlled. The physical and optical properties of the QD-microgel particles are reported and their initial application for optical imaging is explored.

COLL 151

Tailoring the material properties of surface-anchored metal-organic frameworks

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This research evaluates the fundamental physical and chemical properties of surface-anchored metal-organic frameworks (surMOFs) in order to tailor these properties for applications such as energy storage, gas separations, and chemical sensing. MOFs in their most basic form are a class of crystalline, nanoporous materials, commonly fabricated in powder form and composed of metal ion nodes coordinated with organic linker molecules. SurMOFs can be fabricated using sequential, solution-phase deposition in which metal ions and organic ligands are deposited alternatingly on a substrate, which is typically functionalized with a self-assembled monolayer. Utilizing an automated deposition process, we deposit layer-by-layer a range of MOF types with the copper-paddlewheel node structure. We characterize their physical and chemical properties by atomic force microscopy, infrared spectroscopy, ellipsometry, and contact angle goniometry. Using these characterization techniques, the growth mechanism of the films has been investigated for various substrates (i.e. Au, Ge, SiO₂) with different head groups of the self-assembled monolayer (i.e. -COOH, -OH). Film durability was tested in several solvents to explore the chemical stability and determine an optimal etching process necessary for patterning the film. Post-synthetic modification (PSM) was used to tailor the internal structure of the MOF pores after their fabrication.
Performing PSM on surMOF systems permits tuning of physical and chemical properties for specific applications such as targeted binding or separation. Understanding the full breadth of surMOF properties is critical to harness the potential of this emerging material and to integrate them directly into device structures.

**COLL 152**

**Silver selenide nanoparticles as a gateway to diverse quantum dot compositions**

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Cation exchange is an important process in which one cation is switched out with another cation for the creation of novel materials that could not otherwise be made. In this presentation we describe the use of silver selenide nanoparticles as a base from which to create new nanoparticles. We incorporate trivalent metal cations such as gallium and indium by replacing the silver to create their respective selenides. Indium selenide is a particularly attractive candidate due to its band gap, but it is usually synthesized in very high temperature reactions for an extended period of time. However, the cation exchange pathway allows these particles to be under milder conditions with better control over size and shape. We will present x-ray diffraction, transmission electron microscopy, optical spectroscopy, and elemental analysis results on the product materials to identify them and assess their purity and optical properties.

**COLL 153**

**High-precision measurements of the surface tension and viscosity of high-viscosity liquids using surface light scattering spectroscopy and pendant drop tensiometry**

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Surface tension and viscosity are critical for a wide range of applications, such as the development of chemical propulsion systems that operate in low or zero gravity. Space flight requires capillary-driven propellant management devices in order to control propellant transfer. Both surface tension and viscosity can be determined with high precision using Surface Light Scattering Spectroscopy (SLSS). This technique scatters light off of the thermally excited capillary waves (ripplons), with an rms height of ~1 nm, that perturb any fluid interface. The Doppler spectrum of these ripplons, which can be characterized by SLSS, depends upon parameters such as surface tension and bulk viscosity, via the capillary wave surface response function, a refinement of the classical dispersion equation. However, with fluids of high viscosity such as propellants, it has been difficult to disentangle the measurements of surface tension and viscosity, particularly near critical damping of the capillary waves. Innovative optical design has
increased both the signal and signal-to-noise ratio for SLSS. This enhances measurement accuracy over the entire range of wave numbers, while enabling measurements at higher wave numbers above 1500/cm. To test the capabilities of this technique, we compare SLSS measurements with those of a pendant drop tensiometer, whose surface tension readings are independent of viscosity, using glycerol/water mixtures in order to attain a wide range of viscosity.

COLL 154

Modification of silica surface by Suzuki coupling

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In this work, a new method of synthesis of functionalized materials via surface Suzuki coupling was developed. As starting materials, mesoporous 3-(mercapto)propyl- and dimethylsiloxy-functionalized silica gel were used. On the first step, surface hydrosilylation and hydrothiolation of the alkene group of 4-vinylphenylboronic acid were used for its immobilization on the silica surface. The hydrothiolation catalyzed by AIBN demonstrated better effectiveness and resulted in higher density of surface boronic acid groups. In contrast, hydrosilylation products were unstable in reaction conditions and decomposed with time. Then immobilized phenylboronic acid reacted with aromatic halides in the presence of palladium acetate and cesium carbonate in DMF. The following halides were used in the synthesis: bromobenzene, iodobenzene, 5-bromo-1-indanone, 4-iodoanisole, (4-chlorophenyl)acetic acid, 4-iodobenzoic acid. Obtained functionalized materials were also mesoporous although their surface area decreased after immobilization. Degree of immobilization of organic halides was calculated from increase of carbon contents after the reaction, and for most of halides varied between 25 and 67%. Only 5-bromo-1-indanone was almost unreactive at the reaction conditions. Conversion of surface boronic acid groups with iodobenzene was higher than with bromobenzene. Electrodonating methoxy group strongly reduced degree of immobilization of iodoanisole. The method can be used for the preparation of various functionalized catalysts, adsorbents and composite materials.

COLL 155

Self-assembly of micron-sized polystyrene colloids via Langmuir-Blodgett technique for highly reproducible fabrication of large-area gold microcavity arrays

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Nanosphere lithography (NSL) spans a wide variety of techniques for producing 2D arrays of hexagonal-close-packed (HCP) spheres (typically polystyrene, PS), which act as masks for subsequent fabrication. Our interests are in using these HCP masks on smooth gold substrates to produce large-area ($\geq 1\text{cm}^2$) gold microcavity arrays (AuMCAs) via electrochemical deposition. We have previously shown that AuMCAs are effective enhancers of NIR-to-visible upconversion emission from lanthanide-doped nanoparticles. However, difficulties were encountered in using published NSL techniques to reproducibly generate large areas ($\geq 1\text{cm}^2$) of the PS masks with high-quality, long-range order. Here, we describe the development of a NSL technique utilizing a Langmuir-Blodgett (LB) trough to quickly and reproducibly generate high-quality HCP masks with dimensions $\geq 10\text{cm}^2$. The technique is based on carefully controlled introduction of the PS onto the air-water interface using an inclined ‘ramp’. The pressure at the water surface is adjusted such that the HCP array of spheres is formed spontaneously as the spheres enter the water layer from the ramp. The parameters for the method were developed first at the petri-dish scale and then adapted to the LB trough. The free-standing monolayers were deposited onto hydrophilic gold substrates through automated LB software and monolayer quality was assessed using optical microscopy. This technique was shown to consistently provide large ($\geq 10\text{cm}^2$) HCP masks of the PS with a high level of reproducibility and automation. Masked substrates were then subjected to electrochemical plating to produce large-area AuMCAs to be used as enhancing substrates for lanthanide ion-doped upconversion nanoparticles (UCNPs).

**COLL 156**

**Synthesis of FeCo nanoparticles for magnetic hyperthermia**

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FeCo alloys are soft magnetic materials exhibiting low magnetic anisotropy constant ($K_{Fe_{50}Co_{50}} = 1.5 \times 10^4 \text{J/m}^3$) and the highest saturation magnetisation ($M_s$) among any other metal or alloy (bulk $M_s$: 240 – 245 emu/g). In addition, Co is the only element that increases the $M_s$ when alloyed with Fe (55-65% Fe). These remarkable properties of FeCo nanoparticles (NPs) in conjunction with their high heating rate ensure high potential for biomedical applications, such as magnetic resonance imaging, magnetic particle imaging, magnetic drug targeting and especially magnetic fluid hyperthermia for cancer treatment. However, the synthesis of these NPs remains a challenging task due to their poor chemical stability. Herein we report the synthesis of FeCo NPs by thermal decomposition of organometallic precursors. The synthesis is based on the co-decomposition of $\text{Fe(CO)}_5$ and $\text{Co(n}_3\text{C}_8\text{H}_{13})(\text{n}_4\text{C}_8\text{H}_{12})$ in the presence of ligands under $\text{H}_2$ gas pressure. During this study, we aimed to elucidate the effect of ligands, ligands’ concentration and ratio
on the size, morphology and magnetic properties of the as-prepared NPs. Spherical FeCo@FeO\textsubscript{x}O\textsubscript{y} core-shell NPs were obtained with an average diameter less than 25 nm (Fig. 1), demonstrating high Ms values up to 194 emu/g. Among other techniques, HRTEM, XRD, SQUID and EDX mapping have been used for the determination of structural, compositional and magnetic characteristics of these NPs, as well as magnetic hyperthermia for investigating their efficiency to generate heat.

Figure 1. a) HRTEM and b) HAADF-STEM images showing the core-shell morphology of the as-prepared NPs. c-e) elemental (EDX) mapping of Co, Fe and O, respectively. f) Overlapping of Co, Fe, O maps.

**COLL 157**

**Chemically modified titanium boride nanosheets: High yield synthesis and macrostructure assembly**

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The ability to isolate graphene, a single atom thick layer present in graphite, forms an important milestone in the science of nanomaterials. It not only helped realize the first truly 2D nanomaterial but also motivated the scientific community to explore if other layered materials can also be nanoscaled in a similar fashion. The last decade has been witness to a rapid growth in the research efforts towards achieving an entire
spectrum of inorganic nanosheets analogous to graphene. It is expected that boron nanosheets can present excellent platforms to utilize the versatile science of boron. The experimental discovery of borophene in recent times have added momentum to the 2D boron research front. Metal borides represent a family of strongly bonded layered materials in which boron honeycomb planes are held together by interstitial metal atoms. Their construct, which is isostructural to intercalated graphite, holds utmost promise especially in view of realizing quasi-2D forms of boron. So far, metal borides have been primarily employed for their superior physicochemical properties; for example, titanium boride is a super hard ceramic while magnesium diboride is a well-known superconductor. Scientists have recently reported the delamination of layered metal diborides like MgB$_2$ and AlB$_2$, and have shown that nanosheets obtained from these metal borides are functionalized, but rich in boron. Here, we present the chemical synthesis of boron-based nanosheets from another layered boride, titanium boride(TiB$_2$). The methodology utilizes an oxidative intercalation strategy to delaminate TiB$_2$ and results in the colloidal synthesis of chemically modified boron based nanosheets in ultra-high yield. The nanosheets are characterized by FESEM-EDX, UV-Vis, FTIR, and X-Ray Photoelectron spectroscopy. We also present evidence of the high surface area exhibited by this novel nanomaterial from BET measurements. In addition, these nanosheets can be easily assembled into paper-like macrostructures by vacuum assisted filtration.

NaYF$_4$: Yb, Er upconversion nanoparticles (UCNPs) with an active NaYF$_4$: Yb, Nd shell for dual-wavelength excitation

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Upconversion phosphors produce luminescence at wavelengths shorter than that of the excitation light. Upconversion nanoparticles (UCNPs) have important applications in a variety of fields, including bio-imaging, security printing, and latent fingerprint development. UCNPs composed of NaYF$_4$: Yb, Er convert 980nm NIR excitation to visible green (540nm) and red (650nm) emission. The Yb$^{3+}$ ion acts as the sensitizer in this system, absorbing the 980nm excitation and then transferring the excitation energy to the Er$^{3+}$ sensitizer ion, from which visible emission occurs. There are disadvantages, however, to 980nm excitation in certain applications. For example, the 980nm excitation overlaps an absorbance band of water that is weak, but can still result in unwanted tissue heating in bio-imaging. To address this issue, a so-called ‘active’ shell of NaYF$_4$: Yb, Nd can be added to the NaYF$_4$: Yb, Er core UCNPs. The Nd$^{3+}$ in the shell acts as an alternative sensitizer which absorbs 800nm excitation. The NIR-to-visible emission is then generated by the Nd$^{3+}$→Yb$^{3+}$→Er$^{3+}$ energy transfer sequence. The alternative 800nm excitation wavelength falls within a transparent biological window. For security printing, these dual-excitation particles can also be used to print two different but overlapping images which can be viewed individually using different excitation sources.
In this project, NaYF\(_4\): 18%Yb, 2%Er UCNPs with an active shell consisting of NaYF\(_4\): 10% Yb, 10% Nd were synthesized and characterized. Real-time spectroscopic monitoring of UCNPs synthesis and shell addition enables fine control of the experimental parameters to produce reliable product outcomes. The internal quantum yields and brightness of the nanoparticles using 980nm and 800 nm excitation wavelengths will be analyzed as a function of excitation power density.

**COLL 159**

**Investigating the physical and electrical properties of copper-paddlewheel surface-anchored metal-organic frameworks**

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Metal-organic frameworks (MOFs) are highly porous, crystalline materials consisting of metal ions coordinated to organic ligands that arrange themselves in a complex, scaffold-like structure. Surface-anchored MOFs (SurMOFs) can be fabricated using a sequential, solution-phase deposition method in which the metal ions and organic molecules are alternatingly deposited on a substrate. This substrate is typically functionalized with a self-assembled monolayer that anchors the MOF structure to the surface. Utilizing an automated deposition process, we have fabricated multiple MOF types, each with the copper-paddlewheel node structure. The properties of these systems were investigated by scanning probe microscopy, infrared spectroscopy, ellipsometry, electrochemical impedance spectroscopy, and cyclic voltammetry. These techniques reveal the film growth mechanism, structure, and electrical properties. The layer-by-layer deposition method resulted in conformal film growth for two systems via a Van der Merwe growth mechanism, resulting in a smooth film morphology for both MOF types. For one of our systems, electrochemical impedance spectroscopy demonstrated low electronic conductivity hypothesized to be due to topology and density. Porosity of systems was confirmed by cyclic voltammetry methods. This fundamental research into the formation of the foundational layers of these surMOF systems is essential to develop design rules for the integration of these promising materials into real-world applications.

**COLL 160**

**Antibacterial coating on aluminum alloy: SERS detection**

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This research demonstrated the surface alteration of Aluminum alloy. Aluminum 2024-T3 alloy was chemically modified with ZnO nanorods (ZnO-NRs) and silver
nanoparticles (AgNPs). The modified composite materials assessed for antimicrobial properties and SERS detection of toxic molecules. The morphologies of the fabricated composites characterized by scanning electron microscopy (SEM), the elemental components are determined using energy dispersive X-ray line analysis (EDX), TGA, XRD and Raman Spectroscopy.

**COLL 161**

**Switchable single-walled carbon nanotube–polymer composites for CO\textsubscript{2} sensing**

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There has been a growing interest in the detection and monitoring of CO\textsubscript{2} in various fields for industrial concerns and for high food quality packaging. The air quality in the workplace is closely related to the indoor CO\textsubscript{2} concentration. In the food packaging, CO\textsubscript{2} generated by the microbial metabolic activity is one of the food spoilage indicators. Monitoring of CO\textsubscript{2} levels in the foods packed with modified atmosphere packaging (MAP) is also required to ensure the food quality and predict the shelf life. Herein, we report a surface-immobilized chemiresistive CO\textsubscript{2} sensor based on single-walled carbon nanotubes (SWCNTs) noncovalently functionalized with a CO\textsubscript{2} switchable copolymer containing amidine pendant groups that transform into amidinium bicarbonates in response to CO\textsubscript{2}. In the presence of CO\textsubscript{2} under humid conditions, the generated amidinium bicarbonates from the polymer wrapping increase the concentration and/or liberate the hole carriers in the nanotubes, thereby increasing the net conductance of the sensor. The amidinium moieties revert back to the amidines when purged with a CO\textsubscript{2}-free carrier gas with a reversible decrease in conductance. We also demonstrate the sensor performance at various RH values and CO\textsubscript{2} concentrations and its selectivity to CO\textsubscript{2} over the other atmospheric gases such as O\textsubscript{2} and Ar.

**COLL 162**

**Fabrication and application of aluminum nanocrescents for surface enhanced infrared absorption spectroscopy**

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Plasmonics, the phenomena resulting from light interactions with nanoscale structures, is an active field for a wide variety of applications. By varying the plasmonic material, size, and geometry, the nanostructures can be tuned to interact with various wavelengths of light. The noble metals gold and silver are commonly used but can be costly to fabricate. Aluminum is a cost-effective alternative to the noble metals.
However, aluminum's readily forming native oxide layer does present a challenge as it can complicate fabrication but can act as a protection for the structures. Here we fabricate aluminum nanocrescents using an inexpensive, scalable, and parallel technique to investigate their utility as substrates for surface-enhanced infrared absorption spectroscopy. We show that aluminum is an affordable alternative to gold and silver and performs at the same level as gold and silver at IR wavelengths, a region that aluminum is not typically used in, and investigate the differences in line shapes of alkyl stretches between aluminum and gold substrates. Aluminum also shows great promise in other applications due to its high tunability such as; refractive index sensing for biological molecules, photocatalysis, and photovoltaics.

**COLL 163**

Identifying critical parameters of silica coating of silver nanoparticles using ruggedness test

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Optical properties of silver nanoparticles is an important characteristic of these colloids and a way to preserve them when exchanging nanoparticles from one media to another is to coat them in silica. In this work we are trying to identify the critical parameters of silica coating using a ruggedness test. Using a Plackett-Burman factorial design with seven factors, we explored nanoparticle aging time, concentration of nanoparticles, concentration of vitreophilic agent (APS = 3-aminopropyl trimethoxysilane), concentration of silica precursor (TEOS = tetraethyl orthosilicate), concentration of catalyst (DMA = dimethylamine), incubation time in APS and silica condensation time. To quantify the critical parameters we measured the thickness of the silica shell using transmission electron microscopy and to judge the preservation of the optical properties we measured the LSPR (localized surface plasmon resonance). Controlling the optical properties of nanoparticles will allow us to incorporate them in many applications.

**COLL 164**

Novel statistical analysis of Langmuir monolayers

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Langmuir monolayers are commonly used to study the interactions of small molecules and proteins with lipids at the air-water interface. However, these experiments can be
plagued by variability, including inconsistency within the field for some of the analysis methods. To compensate, we analyzed data obtained from compression isotherms of Langmuir monolayers we previously collected using two different methods; the current method most commonly used in literature (compression modulus) and a novel statistical method using inflection points. Our novel method is comparable to the current method.

COLL 165

Manipulating plasmon resonances in In$_2$O$_3$ by bandgap tuning and dual-doping

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Controlling plasmonic properties in semiconductor nanocrystals is a rapidly expanding field of research. These properties can be controlled by adjusting the overlap between the conduction band and donor orbitals. To date, tuning of plasmonic behavior has been achieved in In$_2$O$_3$ by changing the aliovalent dopant from Sn(IV) to Mo(IV), Ce(IV), Ti(IV), and Sb(V) where changes in the effective mass ($m^*$) and carrier concentrations are observed. The ability to tune the plasmon frequency offers potential applications in optoelectronics and sensing. Here we present the tuning of the plasmon frequency of tin(IV) indium oxide nanoparticles through the near-IR by doping with gallium(III). Doping with gallium(III) results in fine-tuned control of the resonant frequency, as well as well-defined Vegard behavior in the nanoparticles. The LSPRs and optical band gaps are characterized by UV-Vis-NIR spectroscopy, while the crystal structure and Vegard behavior are studied via pXRD.

COLL 166

Multi-functional coatings formed from the electrostatic self-assembly of glycerol-based carbon nanoparticles and Moringa oleifera Cationic Protein (MOCP)

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Electrostatic layer-by-layer (LbL) self-assembly of multilayer films has been the focus of many recent research efforts to prepare novel coatings, and a wide range of functional properties can easily be obtained through the simple alternate adsorption of oppositely charged polyelectrolytes in solution. The use of naturally occurring and sustainable materials has become increasingly used in water purification as an economical means to produce potable water in the underdeveloped world. In this work, we combine these ideas through the synthesis of LbL films using glycerol-based negatively charged colloidal carbon particles and the positively charged Moringa oleifera cationic protein (MOCP). The carbon nanomaterial has been shown in our laboratory to have the enhanced ability to adsorb pollutants including lead, cadmium and organic dyes, and the MOCP is known to have anti-microbial properties, reduce turbidity and adsorb heavy
metals. Characterization of the composite films included the investigation of factors that affect film growth, topography, composition, and stability using techniques including UV-vis spectroscopy, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). Results showed that the film thickness and structure depended on the ionic strength used in film deposition. SEM indicated relatively uniform coatings, exhibiting some globular formation. The practical use of these coatings was evaluated by forming films on common quartz sand and results showed an enhanced ability to remove lead, cadmium and methylene blue dye contaminants. The anti-microbial potential of these coatings was evaluated using coated sand and testing with a non-pathogenic form of *Escherichia coli* using simple bacterial culture techniques.

**COLL 167**

**Carbon-dots-based biosensors for the selective detection of biomarkers**

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It is of great interest to modulate the fluorescence response of nanomaterials to target molecules in the field of sensing and imaging. Herein, we present a simple approach based on the solvothermal reaction of catechol molecules for the synthesis of carbon dots (CDs) with different electronic structures for the selective detection of biomarkers. The obtained CDs had an amorphous structure with a lateral size of 30 nm. The CDs exhibited strong fluorescence in the visible range, and its maximum wavelength was tuned by varying the catechol precursors. The fluorescence of the CDs was then quenched or enhanced in the presence of several biomarkers such as CK-MB, myoglobin, and troponin I. The characteristic fluorescence response of the CDs to the protein biomarkers enabled us to detect them in a simple and selective manner.

**COLL 168**

**Study the energy transfer in organic-inorganic two-dimensional hybrid materials**

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Ultrahigh resolution optical and microscopic techniques used to study the interface of colloidal semiconducting two-dimensional materials (CS2DM) indicates it is possible to optimize the CS2DM into optoelectronic devices to improve their efficiency. The energy transfer between the conjugated polymer, and semiconducting two-dimensional
materials were studied. The band gap of the MoS2 is lowered as a result of electron and/or energy injection from the P3HT. The Ultrahigh resolution optical measurement indicates a great dependence on the thickness of an inert polymer spacer that separated them. The Raman and photoluminescense (PL) measurements accorded well with the optical measurements. However, a red-shift in the PL peak was observed in case of the MoS2-P3HT in absence of the polymer spacer. The amount of shift is decreased by increasing the thickness of polymer spacer. The characteristic Raman bands of the MoS2 are shifted to a higher frequency as the thickness of the polymer spacer increased.

COLL 169

Study of the influence of antifoaming additives on the crude oil/air interface by rheology

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Foaming is observed in the primary oil processing, occurring in gravitational separation vessels, where the separation of the oil/water/gas phases is carried out. The foams generated during oil production are complex systems, making it hard to understand what occurs in the foam layers, due to the complexity of their continuous phase. To understand the surface viscoelasticity, it is necessary to investigate the rheology of the crude oil/air interface. Therefore, the aim of this work was to study the crude oil/air interface of different crude oil samples and different antifoaming products using the BiCone accessory.

The tests of the foam formation in crude oil and the rheology of the crude oil/air interface were performed with or without the presence of antifoaming additives. In this study, commercial silicone-based antifoaming agents and formulations composed of a nonionic surfactant based on poly(ethylene oxide) were used. The tests of the foam formation in the two crude oil samples were carried out according to the method described by Fraga\textsuperscript{1} and Rezende\textsuperscript{2}. The rheological properties of the interfacial films of the crude oil/air systems were determined with a Haake MARS 60 rotational rheometer using the BiCone accessory. The main objective of this study was to observe the influence of the antifoaming formulations on the values $G'$ and $G''$ (elastic modulus and viscous modulus, respectively) of the interfacial films, since these properties are very important to understand the antifoaming action mechanism at the crude oil/air interfacial layer. In all the tests, the crude oil samples, with or without the antifoaming formulations, were left in the accessory for 17 hours.

The study reported here showed that rheology measurements of the crude oil/air interface utilizing the BiCone accessory can be correlated with foam formation tests of crude oil samples.

COLL 170
Electrochemical scanning tunneling microscopy studies on the adsorption and assembly of benzenecarboxylic acids at electrode/electrolyte interfaces

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Self-assembly of benzenecarboxylic acids on well-defined noble metals have been intensively investigated using surface sensitive techniques such as scanning tunneling microscopy (STM) - a powerful tool in the study of supramolecular chemistry - the chemistry of the non-covalent intermolecular bonds. However, most studies were focused on the formation of nanostructures via benzene-tricarboxylic and benzene-dicarboxylic acids, which are composed of multiple numbers of carboxylic acid functional groups, allowing to form long range ordered molecular array through COOH-mediated intermolecular hydrogen bonds. Two dimensional nanostructures of benzoic acids comprising of a single carboxylic acid functional group on the phenyl ring at metal-electrolyte interfaces were rarely reported using scanning tunneling microscopy (STM) because only one carboxylic acid for each benzoic acid is available to form intermolecular hydrogen bonds, making it difficult to construct long range ordered nanoscale architectures. In the present work we employed scanning tunneling microscopy (STM) in combination with electrochemical techniques to explore the adsorption and phase formation of benzoic acids at Au(111)/electrolyte interfaces. Our experiments show how electrolyte, molecular concentration, electrochemical potential, co-adsorption of aqueous ions affect the adsorption and self-assembly of benzoic acids. Effect of parameters (electrolyte ions, concentration, potential) revealed in this study will provide valuable information in the formation of molecular adsorption, self-assembly, materials, corrosion inhibition, and molecular devices.

COLL 171

Programmable self-assembly of functionalized tricarbazolo triazolophane macrocycles at interfaces

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Molecular self-assembly at surfaces offers an efficient route to highly-ordered films that can be programmed for a variety of applications. However, the success of these materials depends on the ability to program intermolecular interactions in molecular sub-units to self-assemble into highly organized architectures and thin films. A prototypical molecular platform of tricarbazolo triazolophane macrocycles (tricarb) was programmed with peripheral alkyl units and other functional groups to steer 2D packing
and 3D stacking. The supramolecular assembly is characterized by scanning tunneling microscopy at the solution-graphite interface. Tricarb selfassembles into several 2D structures through non traditional hydrogen bonds between the triazoles and carbazoles as well as van der Waals interactions. Tricarb co-facial stacking is governed by π–π stacking and dipole interactions. Alterations in the alkyl chain lengths, solvent composition, temperature, and solute concentration vary the 2D organization between several states with different tricarb-tricarb interactions and packing densities with one state lacking long-range order. While macrocycles are bound via hydrogen bonding, varying the peripheral alkyl chains controls self-assembly. Altering the solvent composition enhances stacking and changes transition rates between states. Understanding the programmability of these variables allows for control over the molecular self-assembly for future thin film use and study.

Figure 1. Scanning tunneling microscopy images of two phases of tricarbazolo triazolophane macrocycles

 COLL 172

Synthesis mechanism of mesoporous titanium dioxide from industrial titanyl sulfate solution

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Industrial titanyl sulfate solution was used as inorganic titanium source to prepare mesoporous titania via composite template synthesis route, using
cetyltrimethylammonium bromide and tri-block copolymer (EO_{20}PO_{70}EO_{20}) as structure-directing agents under high acidic conditions. The precursor was prepared by controlling the hydrolysis and condensation rate of industrial TiOSO_{4} solution by adjusting pH. Mesoporous titania was obtained after template removal by ozone oxidizing, multi-step extraction and then by step-by-step calcination. The results showed mesoporous titania was hexagonal mesophase, with BET specific surface area of 234.6 m^{2}/g, average pore diameter of 3.28 nm, thermal stability and with anatase nanocrystalline phase. The formation process of mesoporous titania was via static (S+I^-) and hydrogen bond interaction (N^0I^0) at the interphase of the composite surfactants. Titanium primary hydrolyzed colloid particles aggregated around the micelle, and then condensed to form the mesostructure. The whole process could be described as cooperative formation mechanism for mesoporous titania.

![Fig.1 Low angle XRD pattern for the synthesized titania](image)
Fig. 2 Sketch map of mesoporous titania formation mechanism via supramolecular induced hydrolysis of industrial TiOSO$_4$.

**COLL 173**

Analyzing molecular structure of liquid crystals to develop wavelength independent films to mitigate laser attacks on aircraft

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Laser attacks on aircraft have become a prevalent occurrence over recent years, and present significant challenges to pilots of commercial, military and private aircraft during critical stages of flight. These attacks are seen as a distraction, cause flash blindness, or result in permanent eye damage, endangering the lives of the pilot and crew. Previous work has shown to provide incomplete performance as wavelength dependencies limit the effectiveness of the system. In an effort to move past a wavelength dependent solution, this work focused on taking advantage of the polarization and absorbance properties of liquid crystal (LC) technologies to block intruding laser light. In the creation of a cell, the surface of Indium tin oxide was prepared via controlled polishing, influencing the LC to align in a planar orientation when applied voltage creates an electric field within the cell. As laser light permeates the LC, its power is reduced via the following dissipation pathways; absorption of the laser’s energy, scattering of the laser light when in crystal phase, and an interaction with linearly polarized light. If polarization of the laser and LC are parallel, the LC relies on the ability to reflect light in crystal phase. If these polarizations are perpendicular, roughly 90% of the lasers power is blocked regardless of wavelength. The only observable wavelength dependencies are more efficient blocking against wavelengths the respective LC absorbs. This study seeks to analyze how blocking efficiency is impacted by the molecular structure of varying LC’s.

**COLL 174**

Probing the influence of surface dipoles on the structure of contacting liquids with sum frequency generation spectroscopy

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Interactions at the solid-liquid interface have a large impact on the macroscale wetting properties of thin films. Surface-specific sum frequency generation (SFG) spectroscopy, one of a limited number of techniques having the capability to probe such interfaces, generates a surface vibrational spectrum that is sensitive to molecular structure and can
be used to determine the orientation of molecules at the interface. This presentation utilizes SFG spectroscopy to study the interaction between liquid acetonitrile and selectively fluorinated self-assembled monolayer (FSAM) interfaces generated by the adsorption of \( \text{CF}_3(\text{CH}_2)_{17} \text{SH} \) and \( \text{CD}_3(\text{CF}_2)_6(\text{CH}_2)_{10} \text{SH} \) on gold. The C–N and C–H stretching regions, 2000–2300 cm\(^{-1}\) and 2800–3050 cm\(^{-1}\), respectively, were used to probe the solid-liquid interface of the FSAMs in contact with acetonitrile. The appearance of positive- or negative-pointing peaks in the SFG spectrum of acetonitrile as a function of the variation in the terminal group of the FSAMs could be attributed, to a first-order approximation, to the presence of dipoles at the top of the films. Thus, the orientation (up or down) of the acetonitrile peaks were ascribed to changes in the FSAM dipole direction. Coherent molecular spectroscopy was used as a direct probe of this effect by examining the differences in the SFG spectra to determine the relative orientation of acetonitrile with respect to the underlying SAM and, therefore, provided evidence for the dipole-influenced wettability behavior of these unique surfaces.

**COLL 175**

**Silver nanowire/graphene oxide conducting films on antireflective/superhydrophilic substrates**

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Silver nanowire films have been shown to be effective as a replacement for Indium Tin Oxide (ITO) in optoelectronic devices. ITO is a brittle oxide which requires high processing temperature, incompatible with flexible substrates. Thin films of metal nanowires are flexible and require low processing temperatures, with transmittance (T) and sheet resistance (\( R_s \)) on par with ITO films. Nanowires of high aspect ratio and diameters < 30 nm have produced the best quality films. These systems can easily oxidize and have surface roughness which reduce the efficacies of produced devices. By coating these devices with graphene oxide, the metal nanowires have protection from ambient oxygen and the roughness is decreased, however transparency is reduced. By first generating an antireflective coating of silica nanoparticles and poly(allylamine) on the surface using a layer-by-layer approach, the transmittance can be boosted to above 92% T against a background of air with \( R_s < 20 \) Ω/sq. This transmittance is greater than that of pure glass and plastic substrates. The processability of substrates can be simultaneously improved by the antireflective coating. The change in contact angle of silver nanowire dispersions decreased from 32° to 0° with instantaneous wetting.

**COLL 176**

**Synthesis and nanopatterning of core-shell nanoparticles encapsulated with porphyrins**
A method for preparing core-shell metal nanoparticles that are encapsulated with porphyrins using strategies based on Si-O coupling will be introduced. Our efforts build upon a wealth of information that is already known since there is considerable precedent for studies of the synthesis, structures and properties of porphyrins. Our protocol for synthesis of porphyrin encapsulated nanoparticles is based on chemical reactions with silicon tetrachloride in a “one pot” reaction, covalently linking macrocycles through Si-O bridges directly to the center of macrocycles. Chromophoric porphyrins provide a way to introduce interesting electrical and photophysical properties to nanomaterials. The planar molecules of porphyrins form a shell surrounding the metal nanoparticles in which the macrocycles are oriented in layers with a cofacial configuration following the curved geometry of the central core, analogous to an antenna. We anticipate that the 3D geometry of core-shell nanoparticles with covalently bound porphyrins will exhibit unusual properties, such as signal enhancement for generating photocurrents. As a consequence of the covalent Si-O bonding motif, we predict that the linkages between molecules and substrates will be robust and will resist the effects of oxidation and heat. The Si-O binding strategy further provides the capability of controlling the orientation of the macrocycles through axial interconnections between a central Si atom inserted within the macrocycle. This design has been referred to as a “shish kebob” assembly, in which molecules are skewered together by Si-O-Si bridges. The chemical nature of surface linkages is a crucial variable for designing heterojunctions in configurations for molecular electronics. Colloidal lithography was used to generate circular ring patterns of porphyrin/gold nanoparticles to generate a periodic, well-defined arrangement for studies with atomic force microscopy. We are working to uncover new information about the correlation between composition, size and the electronic/photonic properties of the newly synthesized nanomaterials.
Selective electrodeposition of polyaniline on transparent indium tin oxide electrodes using magnetic nanoparticles and magnet arrays

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Electrically conducting polymers, such as polyaniline, have numerous applications, including use in energy storage, medicine, sensors, separations, and smart devices. In many of these applications, the conducting polymer needs to be deposited on a substrate in a certain pattern dictating its function. Current methods of patterning these materials have several limitations, including high complexity steps requiring specialized instrumentation. Here, we present a simple patterning technique that uses magnetic nanoparticles and a magnet array to electrochemically deposit polyaniline on desired regions of an indium tin oxide electrode. This method utilizes the strong interactions between magnetic nanoparticles and magnets, as well as various surface chemistry modifications, to achieve the desired patterns. In addition, a second material can be deposited on the electrode in the unpatterned regions. Taken together, our results provide a proof-of-concept for a general method of patterning conductive polymers on transparent and flexible substrates.

COLL 178

Preserving silver nanoparticle color in solutions and films using silica coating

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Silver nanoparticles can be synthesized to become certain colors in solution. Methods have been introduced to properly coat these nanoparticles with silica and transform them into films maintaining their solution color. Coating gold takes 2-3 hours, but the reagents are not silver nanoparticle friendly. Silver takes many steps and 2-3 days to coat, which can be costly at large amounts. A hybrid method between the silver and gold coating methods was tested, taking 2-3 h to completely coat silver nanoparticles. The color was monitored in solutions and films using UV-vis, and with TEM, the formation of the nanoparticle and silica shell were monitored. Color was preserved from solution to film. Reproducing the silver nanoparticle colors could make the design of sensors environmentally friendly and cost-efficient.

COLL 179

Novel patterning method of silver nanowire-based transparent electrode by selective hydrophilic treatment of substrate
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Transparent electrodes are essentially used in many optoelectronic devices such as display, organic solar cells, touch screen. Although Indium tin oxide (ITO) is the most widely used transparent electrode materials, the needs of alternative transparent electrode materials was suggested due to the price instability by the limit of indium reserves, expensive process through vacuum process, and difficulty to apply to wearable device because of material limit. So, alternative transparent electrode materials such as CNT, graphene, conductive polymer, and metal nanowires have been studied. Among them, the metal nanowires is evaluated as the most suitable alternative transparent electrode due to excellent electrical, optical and mechanical properties. But, when we apply silver nanowire (AgNW)-based transparent electrode to an optoelectronics, a leakage current can be generated due to high surface roughness. In order to solve these problems, we can decrease surface roughness by embedding on a polymer or overcoating transparent materials on AgNW-based electrode. And, to apply AgNW-based electrode to devices, a patterning process is essential. Generally, AgNW-based transparent electrode is patterned by using a photolithography technique or directly irradiating the laser to etch AgNW. However, these patterning techniques are complicated and required expensive process cost. So, researches of new patterning techniques are necessary. In this study, we fabricate embedded AgNW-based transparent electrode to solve problem of high surface roughness. Then, we control the surface energy of substrate by selective hydrophilic treatment, thereby we control the adhesion between the AgNW and substrate to form the patterned AgNW-based electrode.

We selectively treated with a UV-Ozone system to control the surface energy of the substrate. The selective surface treatment can control the adhesion between the substrate and AgNW, and when the photo-curable polymer is peeled off, we can fabricate the patterned AgNW-based transparent electrode. So, we fabricate a pattern with line width of at least 50μm. In order to apply AgNW-based electrode to optoelectronic devices, we fabricate the patterned AgNW-based electrode by hydrophilic treatment, we apply AgNW-based electrode to organic photovoltaics. Compared to conventional ITO-based organic photovoltaics, the organic photovoltaics using the patterned AgNW-based electrode exhibited similar or better characteristics.

**COLL 180**

**Dewetting conditions and morphologies of poly(vinyl alcohol) thin films fabricated on polydimethylsiloxane substrates**

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A thin film can be stable, unstable, or metastable depending on the nature of the thin film, the underlying substrate, and their interactions. Continuous thin films are advantageous in some applications while controlled dewetting is desirable in others.
Understanding the conditions under which dewetting takes place and the corresponding dewetting morphologies is critical in thin film applications. Polydimethylsiloxane (PDMS) is a unique polymer with applications in a variety of fields. Due to its hydrophobicity, however, applications of PDMS in some areas are limited. Poly(vinyl alcohol) (PVOH), is a water-soluble polymer. In this research, PVOH thin films were fabricated on PDMS via spin casting to improve the substrate’s hydrophilicity. This study investigated the conditions under which PVOH thin films dewet on PDMS substrates and the dewetting morphologies. Contact angle goniometry, ellipsometry, optical microscopy and atomic force microscopy were used to characterize the films. Linear relationships have been established between log(PVOH thickness) and log(spin rate). The proportionality constant, k, is greatly affected by PVOH concentration. We have demonstrated that the stability of the PVOH thin films is correlated to the k value with k < -0.5, -0.5 < k < 0, and k = 0 corresponding to wetting, partial dewetting, and complete dewetting, respectively. This correlation has not been previously reported. Dewetting morphologies including droplets as well as fractal features largely depend on PVOH degree of hydrolysis.

**COLL 181**

**Amphiphilic peptoid polymers for directing the assembly of gold nanoparticles at the oil-water interface**

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Two dimensional (2D) gold nanostructures are extensively studied due to their interesting optical and electronic properties. These properties are highly dependent on the specific arrangement of the nanostructures within the 2D architecture. Many strategies have been employed to control the precise arrangement of gold nanostructures in two dimensions, including the self-assembly of gold nanoparticles at fluid interfaces. This inexpensive and simple method is particularly useful, as the 2D patterning of nanoparticles at the interface can be tuned through careful selection of the nanoparticle ligand and the addition of surfactants. However, many challenges still remain in producing well-ordered, uniform, and stable 2D nanoparticle arrays via self-assembly at fluid interfaces. Here, we show that amphiphilic peptoid polymers are promising surfactants to direct the assembly of hydrophobic gold nanoparticles at the oil-water interface. In particular, surface tension measurements indicate synergism in the assembly of the water soluble peptoid and the toluene soluble nanoparticles at the toluene-water interface, thus demonstrating significant interactions between the nanoparticle ligand and the peptoid hydrophobic groups within the interfacial assembly. SEM and AFM images further indicate ordering of the nanoparticles within the deposited composite assemblies.

**COLL 182**

**Examining the effect of functional groups on ligand substitution dynamics**
With the growing popularity of semiconductor nanocrystals, it has become increasingly important to understand how their surface chemistry can be altered to control the ways in which nanocrystals interact with their environment. In this study, in order to substitute insulating, native ligands for shorter ligands, a series of bifunctional molecules with a consistent thiol anchoring group and changing terminal functional group were introduced into as-synthesized nanocrystal solutions. The optical properties of the nanocrystals were measured as the new ligands were added to observe fluorescence quenching, which is characteristic of thiol ligand binding. The extent of ligand exchange was quantitatively analyzed using \(^1\)H NMR. The \(^1\)H NMR peaks of free ligands and nanocrystal-bound ligands were monitored and used to calculate the equilibrium constant of ligand exchange. These data were used to gain insight into the possible ligand exchange mechanisms and to understand how the affinity of binding is influenced by ligand functional groups and the availability of protons in solution.

**COLL 183**

**Road to custom engineered nanocrystal surface chemistry: Changes without exchanges**

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Ligand exchanges are useful processes that can alter the chemical and optoelectronic properties of colloidal quantum dots (CQDs) to broaden their functionality. This exchange requires the original ligand to be removed from the CQD surface in order to replace it with a more desired ligand for a specific application. However, while straightforward in thin films, colloidal ligand exchanges often result in decreased solubility and PLQY, and can often be rather finicky processes. We present here our initial findings concerning an alternative technique for changing the organic matrix around a CQD, which we call “on-particle ligand modification”. In this process, QDs are synthesized with a novel glycol-functionalized ligand in place of the typical surface-bound molecules (oleic acid, etc.). This ligand is then oxidatively cleaved after cleanup while remaining attached to the particle’s surface. In this work, oxidation of oleic acid formed its glycol, 9,10-dihydroxystearic acid (DHSA), which was then utilized in a highly modified synthesis for CdSSe CQDs. New solvent mixtures were developed to account for the increased polarity of the DHSA with respect to typical aliphatic ligands. The DHSA-coated particles were characterized with UV-Vis, NMR, FTIR, and TEM data. Lead tetraacetate (LTA) was then utilized to cleave the surface-bound DHSA molecules to their aldehydes. In the future, this prototype system will be expanded to different unsaturated fatty acid analogs of oleic acid, in which the corresponding glycols will form closer or further from the carboxylic binding group. This will allow for the engineering of
CQDs with intimate final ligand length and surface polarity while (1) retaining the benefits of fatty ligands during for synthesis and (2) circumventing the need for colloidal ligand exchanges.

**COLL 184**

**Mechanical properties of soft samples measured by AFM indentation: Effects of probe shape models**

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Measurements of mechanical properties of soft materials at nano scale have become important in research areas spanning fields from materials science to biomedical engineering and to biology. Atomic force microscopy is one of the most commonly used experimental techniques. This technique is capable of generating maps of elastic modulus with nanoscale resolution. In addition to reporting spatial variation in elastic properties, results of the measurements are often interpreted to indicate variation of elastic modulus with depth for inhomogenous samples. We note that such conclusions might be strongly affected by selection of the probe shape model used in the data analysis. Common approaches use analytically simple models that employ geometrically simple shapes (e.g., paraboloid of revolution). Part of the probe that comes in contact with the sample might deviate considerably from such shapes, resulting in artifacts produced by simple models. In this work we compare results obtained for paraboloidal probe shapes with hyperboloidal and hybrid spherical-conical shapes. Models also include effects of sample adhesion. The developed models are applied to analyze indentation mapping on aligned collagen samples. Indentation results show presence of soft surface layer and we discuss whether such conclusion is model independent.

**COLL 185**

**Polyethylene glycol and RGD immobilized binary colloidal crystal nanostructures as tunable substrates for cell culture**

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The emerging field of biomedical and tissue engineering requires novel surface fabrication approaches to impart advancements for a range of applications viz. medical implants, cell culture tools, regenerative medicines etc. Variation in the topographical
features along with different chemistries has always been a popularly explored strategy to get control over mammalian cell responses. This research work investigates the generation of potential biomaterial surface coatings fabricated with binary colloidal crystal (BCC) layers containing large (L) micro- and small (s) colloidal nano-spheres, thereby giving rise to 2D or 3D surface micro-/nanotopographies. We apply a covalent binding approach to conjugate different chemical entities such as non-fouling polymers (e.g. PEG) or integrin binding RGD peptide, being involved in promoting cellular attachment, to large silica (Si) particles. Afterwards, we utilize a variety of pre-modified Si and smaller sized polymeric particles in different aspect ratios, chemical compositions and varied colloidal layer numbers to generate well-ordered BCC topographical features. A range of physico-chemical characterization techniques including zeta potential, x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were employed to optimize these tunable cell-culture substrates. Four different well-defined BCC combinations presenting cues for controlled bio-interfacial interactions via PEG and RGD were chosen to perform cellular behavioural studies. We used epifluorescence microscopy and found that well controlled surface chemistry of the BCC layers can induce significant impact on the adhesion, proliferation and spreading behaviour of MG63 osteoblasts in conjunction with distinguishable cellular morphology changes. Thus, PEG grafted BCCs can be useful where cell adhesion is needed in a limited and controllable manner (for instance cell spheroids for use in drug screening of controlled differentiation in 3D microenvironments) while RGD grafted BCCs are able to exhibit significantly higher cell count, greater spreading area and induced lineage-specific gene expression.

COLL 186

Reduction of CO$_2$ on early Earth using UV radiation

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Photosynthetic reactions on the early Earth could have contributed to the origin of life by generating reduced molecules to be used by early cells. In an attempt to understand this important process, artificial cell-like structures were created separately with fluoranthene and 1-pyrenecarboxylic acid, two polycyclic aromatic hydrocarbons (PAHs) thought to have been abundant on early Earth to serve as UV absorbers. These PAHs were tested separately for their reduction activity of carbon dioxide (CO$_2$) in an anaerobic chamber, an environment similar to the early atmosphere, with methanol and bicarbonate as electron donor and acceptor. These cell-like structures were exposed to UV light and a decrease in pH was observed, which might signify the reduction CO$_2$/bicarbonate into formic acid or other reduced products. These products were then extracted using solid phase microextraction and were further analyzed using GC-MS to identify any organic products. Better understanding of simple electron transfer reactions
and their contributions to the chemical library of early Earth is a step toward the understanding of the origins of life.

**COLL 187**

**Fabrication and evaluation of hydrophobic anti-icing coating with thixotropic lubricant gel**

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Frost formation and ice accretion present serious issues on a variety of industrial systems. Therefore, the anti-icing coating attracts much attention. Slippery liquid-infused porous surfaces (SLIPS) are one of the ways to suppress frost/ice accretion by removing condensed moisture. However, the durability of SLIPS is a concerning problem due to the migration or evaporation of the infused lubricant.

In this work, we fabricated the robust anti-icing coatings by utilizing the thixotropic lubricant gels. Figure 1a shows the variation of contact angle (CA), sliding angle (SA) and contact angle hysteresis (CAH) on the SLIPS and thixotropic lubricant gels (TLG) with the number of the shower test cycles. The values of SA and CAH increased on the SLIPS after 5 cycles of the shower test, whereas the values of CA, SA, and CAH were almost unchanged on the TLG coated surfaces. As a result, it maintained the wetting property even after 5 cycles of the test. It indicated that TLG is more tolerant than SLIPS because the lubricant loss was suppressed owing to the high stability of TLG. In addition, this durability of water repellent property is expected to contribute to the delay of frost formation (Figure 1b). TLG coating delayed the frost formation (35 min) compared with that of SLIPS (13 min) at –10°C.

![Figure 1](image_url)

Figure 1. (a) Variation of CA, SA and CAH on SLIPS and TLG with the times of the shower test cycles. (b) Time-lapsed images of the frost formation on a bare glass, superhydrophobic surface (SHS), SLIPS, and TLG at 10°C and 50%RH.

**COLL 188**
Venturi effect: A novel way to obtain nanodispersions by solvent displacement

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Nanoparticles (NP) are formed by a turbulent flow that is produced in the throat of the Venturi tube (VT). Taking advantage of this effect, polymeric nanoparticles (PNP) of poly-e-caprolactone and solid lipid nanoparticles (SLN) of monoolein were produced by diffusion of organic phase through the aqueous phase (solvent displacement method). The objective of this study was to evaluate the critical preparative variables to obtain dispersions in the submicrometer size range. Response surface methodology (RSM) was used in order to determine the effect of operating conditions. Central Composite and Box-Behnken designs were used for PNP and SLN optimization. Results showed that the Reynolds number (Re) upper 4000 was necessary for producing turbulence flows that are critical condition to obtain nanoparticles. The turbulence regime is the key to the efficient formation of NP. The process yield (PY) was > 85.0 %, with a mean particle size (PS) < 300.0 nm, polydispersity index (PDI) of 0.2 and zeta potential (ZP) > 25 mV for polymeric and lipid NP. VT method is an innovative and versatile technique for preparing nanoparticles of nanometric size with high process yield through turbulent flow.
Quantifying adsorption of chlorpromazine and clozapine to phospholipid membranes using second-harmonic generation

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Chlorpromazine and clozapine are both used to treat psychotic illnesses. However, patients taking chlorpromazine exhibit more adverse side effects than those taking clozapine, which may be attributed to nonspecific interactions with lipids in the plasma membrane. We used second harmonic generation (SHG) to monitor the adsorption of these two antipsychotics to artificial phospholipid membranes. SHG allowed us to detect adsorption of small molecule drugs without fluorescent labels or extrinsic tags, which could interfere with the adsorption of the drug to the membrane. Artificial phospholipid membranes mimic mammalian plasma membranes and allowed us to control (and increase stepwise) the complexity of the lipid bilayer. We varied head group charge, alkyl chain length, fluidity, and cholesterol content. We studied the antipsychotics under physiologically-relevant drug concentrations and pH conditions. At circumneutral pH conditions, clozapine is neutral in charge while chlorpromazine is cationic. Adsorption data were fit with the Langmuir model; binding constants and relative surface concentrations were determined and comparisons were made for the two drugs. The goal of our studies was to gain knowledge about how the structure of an antipsychotic impacted its membrane-binding properties and to aid in the understanding of the mechanism behind antipsychotic drug-plasma membrane interactions.

Solution-phase synthesis and thermoelectric characterization of n- and p-type tetrahedrite nanoparticles

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Tetrahedrite (Cu₁₂Sb₄S₁₃) composed of earth-abundant elements is a thermoelectric material capable of converting waste heat into electricity. Typically, it is produced by conventional solid-state methods requiring extended reaction times (weeks) at elevated temperatures (>600° C). We developed a modified polyol synthesis that requires only one hour of heating at 220° C to produce high yields (2+ grams) of surfactant-free, nanostructured, and phase-pure tetrahedrite materials. Nanoparticles (50-200 nm) were characterized by powder x-ray diffractometry, scanning electron microscopy, and energy dispersive x-ray spectroscopy. Thermopower, electrical resistivity and thermal
conductivity measurements were obtained to determine figure of merit (ZT) values, which describe the quality of thermoelectric performance. Our solution-phase synthesis outperforms tetrahedrite materials made by conventional methods, and has been shown to successfully incorporate dopants such as Fe, Zn, and Co on the copper-site. N-type behavior in tetrahedrites has not previously been observed. We report the first observation of negative Seebeck coefficient values over a temperature range of 80 K to 310 K for Fe-doped materials. Electrical and thermal transport properties on these samples are provided from 80 K to 673 K. Since thermoelectric devices require both n- and p-type legs, thermal expansion mismatch issues are eliminated by synthesizing tetrahedrite with each electrical behavior.

**COLL 191**

**Investigating nanoparticle-protein interactions with hybrid lipid-coated gold nanoparticles**

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Nanomaterials engineered for biomedical applications are designed to interact with and function in a living host environment. The overall goal is to design nanomaterials that are biocompatible, non-toxic, and that do not undergo biological transformations that result in loss of function and stability. Consequently, there is a critical need to understand, at the molecular and cellular level, nanoparticle biological interactions. More specifically, to study interactions with between nanoparticles and proteins. Thus far, studies have shown that nanoparticle stability is influenced by nanoparticle transformations that occur upon contact with biological environments such as saliva, blood, and media *in vivo*. For example, when nanoparticles are exposed to the bloodstream they interact with opsonin proteins that attach to the surface of the nanoparticles forming a protein corona. This protein-nanoparticle interaction then triggers the phagocytic system that recognizes the protein-nanoparticle species for clearance and then accumulates in the liver and spleen. Concomitantly, this can result in low targeting, uptake efficiency and systemic toxicity. The surface chemistry of the nanoparticles is the driving force behind the formation of the protein corona and aggregation resulting from interactions between nanoparticles and components of the biological media. To achieve stable systems, we must fill the gap in knowledge regarding our understanding of how the architectural design of nanomaterials influences nanoparticle-proteins, stability, and toxicity. Here we will describe the synthesis of hybrid lipid-coated nanomaterials with varying sizes, surface chemistry, and charge to determine how these features influence nanoparticle-protein interactions. We will present UV-Vis spectroscopy, dynamic light scattering, and transmission electron microscopy studies of nanoparticle-protein interactions. Through these studies, we expect to harness knowledge that can help overcome translational barriers for their use as drug delivery, cellular labeling, and optical imaging agents.
Investigating adsorption dynamics of serum proteins onto gold nanoparticles

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Gold nanoparticles (AuNPs) have the potential to improve immunodiagnostics, immunoassays, and biosensing. Many emerging biosensors rely on the immobilization of antibodies onto AuNPs due to the optical properties of the AuNPs and the specificity of antigen binding by antibodies. Preferably, the AuNP-antibody conjugate interaction will be stable and strong enough that their interaction will not be affected by exposure to biological systems. However, AuNPs can interact with biological components affecting its reliability and performance. In this research, our group investigated the adsorption interaction of common blood serum proteins (transferrin, human serum albumin (HSA), IgG, Fibrinogen) onto AuNPs and the ability of these serum proteins to displace antibodies from antibody-AuNP conjugates. Our group used nanoparticle tracking analysis (NTA) to study serum protein and antibody adsorption on AuNP by measuring the mean size increase of the functionalized conjugates. Our data show a monolayer of protein was formed at saturation for each protein and the maximum size increase correlated with the protein size. Additionally, adsorption data was best-fit to the Hill-Langmuir equation to extract the adsorption affinity for each protein. Lastly, the ability of blood serum proteins to displace antibodies from the surface of AuNPs was investigated using an enzyme-mediated assay. Preliminary experiments suggest that serum protein cannot displace antibody during one hour of exposure, but prolonged exposure may result in protein exchange. Ultimately, these studies elucidated the differences in blood protein adsorption onto AuNPs and the stability of antibody-AuNP conjugates when exposed to blood protein serums. Results of this work will help to define the capabilities and limitations of antibody-AuNP enabled biosensors.

Sonochemical functionalization of boron nitride nanomaterials

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Boron nitride nanomaterials (BNNTs) and hexagonal boron nitride platelets (h-BNs) have received considerable attention for composite and aerospace applications due to their exceptional properties. Recent advances in synthesis techniques have prompted the production of significant quantities of commercially available BNNTs, but quantification techniques for confirming BNNT sample purity are not capable of
resolving differences between h-BNs and BNNTs. Additionally, matrix compatibilization of BN nanomaterials can be tricky; h-BN can be hydrophilic or hydrophobic depending on orientation, and due to chemical stability BNNTs are difficult to covalently functionalize. In this work, UV/Vis spectrophotometry is used to calculate a concentration calibration curve for h-BN and BNNT samples. We propose a novel method for determining the purity of BNNT samples by comparing the ratio of characteristic stretching and bending peaks in the spectra. We also present novel sonochemical techniques to covalently attach fluoroalkoxy substituents to the surface of BN nanomaterials. Attachment is confirmed via FT-IR, solvent compatibility and the use of x-ray photoelectron spectroscopy (XPS).

**COLL 194**

Hydrogel-stabilized radioluminescent colloidal crystalline arrays: Fine-tuning color characteristics via Förster Resonance Energy Transfer (FRET) pairing

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Fully organic x-ray active colloidal crystalline arrays (CCAs) are encapsulated in hydrogel networks in order to generate thin film devices that may further aid in the efforts to overcome the inherent scattering in optical bio-imaging. Encapsulating these CCAs in a poly(ethylene glycol) methacrylate based hydrogel network has advantages over the liquid system in regards to the stability of the crystal structure. These x-ray active thin film devices are composed of electrostatically stabilized CCAs of monodispersed polystyrene, propargyl acrylate nanoparticles with an encapsulated organic scintillator, trans-stilbene. By post functionalizing the hydrogel with organic dyes such as naphthalimide and rhodamine B via click chemistry, the hydrogel can be tuned to span the full visible spectrum via x-ray induced sequential Förster Resonance Energy Transfer (FRET) pairing. Blue-emitting, x-ray excited trans-stilbene transfers energy to green-emitting naphthalimide which can then transfer energy to red-emitting rhodamine B. While stabilized in the hydrogel film, the CCAs are able to continue exhibiting this x-ray induced FRET and stopband tunability with an x-ray pump. The rejection wavelength of the CCA encapsulated hydrogel can be coupled to the x-ray excited optical luminescence to fine tune color characteristics.

**COLL 195**

Design of cholera toxin B-conjugated gold nanoparticles to target retinal ganglion cells in the eye

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Glaucoma is an incurable disease and is a leading cause of blindness that is projected to affect 76 million people by 2020. The main cause of glaucoma is the degradation of the retinal ganglion cell layer within the eye and unlike other peripheral nerve cells, RGCs are part of the central nervous system and cannot be replaced. Consequently, there is a great need for therapeutic strategies as well as technologies that would enable us to detect the early stages of damaged RGCs before permanent blindness occurs. Currently, OCT is a widely used non-invasive technology used to diagnose and monitor diseases such as glaucoma, age-related macular degeneration (AMD), and diabetic retinopathy. While OCT is able to visualize individual retinal layers at micron scale resolution, it is a poor molecular and cellular imaging technique. While strong absorbing organic dyes enhance OCT contrast there are issues with contrast delivery, visualization in deep tissue, and difficulty tuning them near-infrared region (NIR). Recently, gold nanoparticles (AuNPs) were shown to be potential alternatives to dyes and drug carriers in the eye. It has been demonstrated that enhanced contrast occurs when the central operating wavelength of the OCT matches the surface plasmon resonance (SPR) band of the AuNPs. While this is a great step in the right direction, there is a great need for AuNPs that can bind to specific cells to visualize layers of cells in the eye using OCT. Here we describe the synthesis of hybrid lipid-coated gold nanoparticles with lipids-conjugated to Cholera Toxin B subunit that is known to bind to the GM-1 gangliosides receptors in RGCs. We will present UV-Vis spectroscopy, dynamic light scattering, and fluorescence spectroscopy data to show that the Cholera Toxin B subunit is conjugated to membrane-caped AuNPs. We will also present data evaluating the stability of the cholera toxin-conjugated AuNPs to evaluate the effect of physiological conditions on the stability of the nanomaterials that could diminish or enhance contrast. These nanoparticle platforms when combined with OCT can be used in an in vivo diagnostic for glaucoma to detect early changes in layers of RGCs of patients.

COLL 196

Magnetic microdroplets as a method to extract antibodies from their growth media

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Antibodies are one of the fastest growing sectors of the biopharmaceutical industry. Extraction and purification of antibodies accounts up to 70% of the production cost. The main target of this project is combining ferrofluid and hydrophobin-proteinA fusion protein for extracting antibodies from their growth media by the formation of magnetic microdroplets. Applying high magnetic field on oil-based ferrofluid creates numbers of microdroplets, which means creating large hydrophobic surface area. HFBI-ProteinA is a fusion protein that is able to self-assemble at hydrophobic interface and catch antibodies. These two materials represent the cornerstone of this project. The project combines biological and soft matter physics. The soft matter part has been done at Aalto University, Soft Matter and Wetting research group. The biological part has been done at VTT Technical Research Center of Finland Ltd.
A novel method to extract antibodies from their growth media was developed. This method made progress in the liquid-liquid interface research, which is one of the challenging research areas, especially in the presence of several surface active components. Applying this interface as a functional substrate for biomolecules instead of solid-liquid interface represents a major scientific impact. For industrial impact and to proceed towards commercialization, more work is needed to maximize the efficiency of our method.
Teasing apart how specific features of silver nanoparticles contribute to toxicity

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Silver nanoparticles (AgNPs) are extensively used for their antimicrobial properties in an increasing number of consumer and commercial products and as bacterial agents in the treatment of waste water. Because of their high demand, over 500 tons of engineered AgNPs are produced globally. While the physiochemical properties of AgNPs are important for antibacterial activity these may also influence toxicity and have an impact on human health and the environment. However, studies designed to evaluate the nanoparticle-specific effects of AgNPs have been limited because of their propensity to undergo Ag⁺ dissolution. Consequently, there is a great need to understand how AgNPs with diverse characteristics such as shape, size, and surface coatings impact their interaction with organisms by controlling for the confounding effects of Ag⁺ contribution to toxicity. There is also a need to understand how these physiochemical parameters dictate nanoparticle-biological interactions (NBI’s). Here we discuss the design of hybrid lipid-coated AgNPs of varying shapes and sizes that are differentially shielded from surface oxidation. We will present UV-Vis spectroscopy, transmission electron microscopy, and ICP-MS studies characterizing the stability of the hybrid lipid-coated AgNPs. We will present ICP-MS data evaluating the AgNPs for Ag⁺ ion release and will show that AgNPs that are completely shielded from surface oxidation do not release Ag⁺ ions. The toxicity and distribution of AgNPs in using zebrafish models will also be presented to identify features of AgNPs that drive toxicity, nanoparticle distribution, and NBI’s. These studies will provide valuable information on the toxicity of AgNPs and Ag⁺ ions release into its surroundings while also providing a potential template for designs on safer nanoparticles.

Colloidal synthesis of hexagonal FeIn₂S₄ and its layer-dependent band structures

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Two-dimensional materials, including transition metal chalcogenides (TMDs), have received considerable attention due to their exotic electrical, chemical and physical
properties. Here in, hexagonal FeIn$_2$S$_4$, a new layered ternary metal chalcogenide, will be introduced as one of the emerging candidates of two dimensionally quantized nanomaterials. As it consists of two metal cations and one chalcogenide anions in their unit cell, their properties are expected to be highly complicated. To deeply understand, a comparison study of the structure of as synthesized hexagonal FeIn$_2$S$_4$ with cubic phase FeIn$_2$S$_4$ (c-FIS) was conducted as well as hexagonal ZnIn$_2$S$_4$. The number of layers of hexagonal structure of FeIn$_2$S$_4$ (h-FIS) was controlled by surfactant mediated colloidal synthesis reaction. Finally, the different band structure of each of h-FIS samples were investigated through the optical bandgap and redox potentials from cyclovoltammetry. This study will contribute to unveiling characteristics of ternary metal chalcogenides and developing new applications.

COLL 199

**UiO-66-NH$_2$ on functionalized graphene oxide (GO)**

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To military personnel protective clothing is essential when they are exposed to chemical warfare agents. The active component of protective clothing mainly consists of activated carbon, which is characterized by high specific surface area and variable pore size. However, activated carbon can adsorb only limited amounts of chemical agents, and therefore large amounts of active materials are requieried to provide longer lasting protection. Attention has been moved to metal-organic compounds (MOFs) in recent years. Clusters of un-coordinated metal ions linked vai organic compounds can offer a promising potential for adsorption and further catalytic reaction. Due to its lightweight and nonflammable characteristics, the co-existence of graphene oxide (GO) with MOFs can lead to the emergence of a promising metarial for protection. Herein, the UiO-66-NH$_2$@GO composites were designed and investigated for applications in the degradation of chemical agents as protective materials.

COLL 200

**Surface growth of UiO-66-NH$_2$ on cotton fabric for toxic chemical degradation**

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Direct growth of the metal-organic framework (MOF) UiO-66-NH$_2$ on cotton fabric was successfully demonstrated. By mercerization for increasing the content of surface hydorxyl groups, cotton can be used directly to grown MOF on the cotton surface. We use X-ray diffraction and FT-IR to confirm that crystalline UiO-66-NH$_2$ was produced on the surface of cotton fabric. Characterization of the composite revealed up to 50 wt% MOF loading according to thermogravimetric analysis (TGA). Since the MOFs are located on the surface of the cotton fabric, the composite are capable to efficiently
degrade chemical agents, suggesting a broad range of filtration and decontamination applications.

**COLL 201**

**Investigation of the effects on stability of silver nanoparticles**

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Silver nanoparticles (AgNPs) have unique chemical and physical properties that have drawn a lot of attention for various applications. Many advances have been made to develop synthesis techniques to fabricate AgNPs with properties that permit their desired applications. For instance, morphological control of the AgNPs which often involve the use of surface ligands has contributed to more understanding of their antimicrobial behaviors. Surface functionalization of these nanoparticles partially dictates their interaction with the bacterial/viral cells, which in turn affect their effectiveness. However, in some cases, these surface-modified nanoparticles tend to aggregate in aqueous solution especially in the biological medium due to their high reactivity with bio-molecules. Stability of AgNPs depends on inter-particle behaviors from intermolecular forces between surface ligands, and these behaviors can be affected by surface chemistry, storage conditions, and type of solvent. In this study, we modified the AgNPs with different polymer ligands through the ligand-exchange method. As-synthesized AgNPs capped with poly(vinyl pyrrolidone) (PVP) were exchanged to cover with branched polyethyleneimine (PEI) to make their surface positively charged. The impact of the ligands on materials stability and antibacterial activity was examined and revealed that PEI-coated AgNPs with a positive zeta potential has better antibacterial activity compared to the PVP-coated AgNPs. This study aims to characterize changes in chemical and physical properties of the AgNPs over time and assess how these properties are affected by storage conditions and type of ligand. Understanding the effects on the stability of AgNPs will not only give insights on how to enhance the AgNPs performance in biomedicine but also address the concern that is posed by these materials to environmental and human communities.

**COLL 202**

**Calcium-triggered release of contents from liposomes for drug delivery applications**

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Liposomes have been widely studied in recent years to enhance their properties as a supramolecular drug delivery platform. A key point of advancing liposomal drug delivery would be to control the timing and location of cargo release to maximize drug potency and minimize side effects. Commonly studied triggered release approaches exploit stimuli including pH (passive) and light (active). Here, we present a novel approach for triggering release of contents from liposomes driven by increased calcium at target sites, which plays an important role in biology related to certain diseases. Firstly, a switchable lipid 1 sensitized to calcium was synthesized and incorporated into liposomes. This lipid trigger has a well-known calcium binding headgroup that can induce a conformational change that perturbs liposome membrane integrity and thereby cause content release upon calcium binding. This was proven by fluorescent dye release assays via dose-dependent response correlating with the percentage of 1 in liposomes. Corresponding dynamic light scattering experiments indicated dramatic changes in particle size upon adding calcium to liposomes containing 1. In selectivity studies, calcium provided the greatest release compared to nine other naturally occurring metal cations. Finally, STEM was used to visualize liposome morphology upon treatment of liposomes containing 1 with calcium and significant changes were observed. All of these results showcase lipid switches driven by molecular recognition principles as an exciting avenue for controlling liposome release.

**COLL 203**

**Dopamine surface adhesion via spin casting**

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Polydopamine (PDA) films, formed by oxidative polymerization of dopamine (DA), have a wide variety of applications as they can function as versatile "primers" for further surface modification and attachment. Typically, PDA films are prepared by submerging
a substrate of interest in a basic solution containing DA for an extended period of time, utilizing oxygen in air as the oxidant. In this research, we explored using the facile spin casting method to prepare PDA films on native and functionalized silicon wafers. Sodium periodate was chosen as the oxidant because it is stronger than the commonly used oxygen. All the DA solutions were prepared in acidic acetate buffers to avoid the interference from oxidation by native oxygen. The reaction variables include DA concentration, pH, solution aging time, adsorption time, and surface chemistry. PDA coatings were characterized by contact angle goniometry, ellipsometry, and optical and atomic force microscopy. Additionally, (P)DA chemistry in solutions was monitored by dynamic light scattering and UV-Vis spectrophotometry to correlate with the PDA adhered to surfaces. Our results so far indicate that it is important to control reaction kinetics in terms of solution pH and DA concentration in order to produce thick and homogeneous PDA films - small PDA particles are surface adhesive but do not yield thick PDA films while large particles can improve film thickness but do not readily adsorb to surfaces. Adsorption time was optimized to allow for surface adhesion and to minimize solvent evaporation. The importance of substrate chemistry on the spin-cast PDA film thickness and morphology will also be presented.

COLL 204

Thermoelectric characterization and thermostability of doped-tetrahedrite nanoparticles synthesized by modified polyol process

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Thermoelectric materials, which convert waste heat into electricity, are a potential avenue toward alleviating the current energy crisis. Tetrahedrite (Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}) is a thermoelectric material typically produced by time and energy inefficient solid-state methods. We developed a bottom-up modified polyol synthesis to produce high yields of nanostructured and phase-pure tetrahedrite materials with one hour of heating at 220°C. Nanoparticles were characterized by powder x-ray diffractometry, scanning electron microscopy, and energy dispersive x-ray spectroscopy. Thermopower, electrical resistivity and thermal conductivity measurements produced figure of merit (ZT) values, which describe the efficiency of energy conversion. Our solution-phase synthesis successfully incorporates a wide variety of dopants, including Zn, Fe, Ni and Co on the copper-site, as well as Se on the sulfur-site. These nanopowders have showed improved ZT values relative to compounds fabricated by conventional solid-state methods. Doping Mn and Ag on the copper-site, Bi and Te on the antimony-site, and Se and Te on the sulfur-site is currently underway. Toward integration of these materials into relevant applications, it is necessary to investigate the thermostability of the tetrahedrite materials. Thermostability data as a function of dopant identity and
concentration is underway by characterization with differential scanning calorimetry and thermogravimetric analysis.

**COLL 205**

**Tyrosine-assisted fluorescent gold nanoclusters for sensing Fe$^{3+}$ and Cu$^{2+}$**

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The protein-templated fluorescent gold nanoclusters (AuNCs) utilizing the reduction capability of tyrosine at alkaline condition are well documented. In this study, we synthesized fluorescent AuNCs by employing tyrosine containing tripeptides. In order to better understand the role of tyrosine, we designed and prepared tripeptides, tyrosine-cysteine-tyrosine (YCY) and serine-cysteine-tyrosine (SCY). We obtained blue and red fluorescent AuNCs from YCY and blue fluorescent AuNC from SCY peptides at pH 10 and 70 °C. Synthesized AuNCs for their physical and chemical properties are characterized in UV-Vis absorption, fluorescence, TEM, and dynamic light scattering (DLS). It is found that the fluorescence of blue-emitted YCY- and SCY-AuNCs is quenched with concentration of Fe$^{3+}$ and Cu$^{2+}$ in a wide linear range, but optical signal of the red-emitted YCY-AuNCs are stable in 13 different metal ion solutions. Interestingly, YCY-AuNCs exhibited higher responsiveness to Fe$^{3+}$ than SCY-AuNCs presumably due to its enhanced aggregation propensity under the existence of Fe$^{3+}$. Details of the fluorescence quenching mechanism is being studied to understand the fluorescence response of each AuNCs to Fe$^{3+}$ and Cu$^{2+}$ ions.

**COLL 206**

**Synergistic oxygen generation of manganese ferrite and ceria nanoparticles potentiates M2 polarization of macrophages for rheumatoid arthritis treatment**

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Macrophage polarization from pro-inflammatory M1 phenotype to anti-inflammatory M2 phenotype has been considered as a promising therapeutic strategy to treat inflammatory diseases including rheumatoid arthritis (RA). M2 polarization of macrophages in joints with RA can be induced by overcoming hypoxia and scavenging reactive oxygen species (ROS). Herein, we develop manganese ferrite and ceria nanoparticle-anchored mesoporous silica nanoparticles (MFC-MSNs) that synergistically scavenge ROS and produce oxygen for M2 polarization of macrophages.
in RA model. MFC-MSNs exhibit the synergistic effect on O$_2$ generation due to hydrogen peroxide decomposition ability of manganese ferrite NPs and hydroxyl radical scavenging ability of ceria NPs, leading to efficient M1 to M2 macrophage polarization in both *in vitro* and *in vivo* model. The inflamed synovial joint of RA-suffering rat model was successfully oxygenated by intra-articularly administered MFC-MSNs, showing the excellent therapeutic effect on RA. These findings suggest an enormous therapeutic potential of this novel platform for M2 polarization of macrophages in various inflammatory disease models.

COLL 207

Monitoring reactive oxygen species production at the single DNA level

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Oxidative DNA damage is a cause for cell death, cancer, and diseases. DNA damage is usually tracked at the cellular level by monitoring reactive oxygen species (ROS). Moving to the single DNA level often gives new insights into reactions that are missed in ensemble studies. Thus, it is advantageous to move ROS monitoring to the single molecule level. In this study we track the ROS produced by POPO-1, an intercalating DNA stain which causes photocleavage of DNA, through activation of CellROX Green. CellROX Green is a commercially available fluorescent DNA stain which is only fluorescent after reacting with superoxide or hydroxyl radicals. This allows us to track ROS production from POPO-1 in real time. This technique should be extendable to track ROS production from other sources at the single DNA level.

COLL 208

Validating Raman spectroscopy for the detection of surface molecules on silver nanoparticles

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Recent studies have focused on the ability of silver nanoparticles to enhance the Raman spectra of molecular compounds, but not the signal of the molecules which inherently surround the particle. The signal of these compounds (PVP, ascorbic acid, and PVA), though weak, may be used to track changes in the molecules present at the particle surface. The validation of the Raman spectroscope using relevant standards was followed by SERS investigations of various stages of nanoparticle film production. Changes in the ratio of spectral peaks were observed, suggesting a connection between the ratio and particle size, concentration, and PVA content in films. By better understanding the surface properties of nanoparticles, a clearer picture of how particles interact with each other and other compounds may be generated.
Gold nanoparticle colorimetric detection of estrogen and estrogen mimics

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Gold nanoparticle (AuNP) based colorimetric biosensors display ease of use and high sensitivity. 17-beta-estradiol, an endocrine disrupting chemical (EDC), has been found in natural water sources and in wastewater effluents within the range of 0.2 to 3 mg/L. We developed a gold nanoparticle based sensor that incorporates a previously identified DNA-aptamer for 17-beta-estradiol which was split in two segments P1 and P2. The respective segments P1 and P2 were conjugated to the surface of 10 nm AuNPs respectively. In the presence of 17-beta-estradiol, the particles aggregate, and a color change from red to purple was observed, with a limit of detection of 0.05 ng/ml.

Preparation of a glycerol-based carbon / magnetic iron nanocomposite for the removal of contaminants in aqueous systems

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With increases in population and industrialism in the last century, clean water sources have become increasingly scarce, a situation most drastically felt in third-world countries. There is an ever-increasing need for research into the development of new, sustainable, and inexpensive materials for use in water purification. In this study, we report the development of a novel magnetic carbon/Fe_3O_4 composite for the efficient removal of lead, cadmium and organic dyes. The simple acid dehydration of glycerol was first used to produce carbon nanoparticles which were then co-precipitated with Fe^{2+} and Fe^{3+} under basic conditions to produce a magnetic carbon nanocomposite. Composite samples were analyzed by several techniques including scanning electron microscopy (SEM), attenuated total reflectance infrared spectroscopy (ATR), and thermal gravimetric analysis (TGA). SEM analysis indicated that the magnetic composites were precipitated as micron-sized platelets covered with nano-sized spherical particles, with a diameter of less than 50nm. This material was found to be an effective adsorbent for Pb^{2+}, Cd^{2+}, methylene blue with maximum adsorption values of over 100 mg/g, 70 mg/g and 300 mg/g respectively. The adsorption was, however, found to be pH dependent with decreasing adsorption amounts in more acidic solutions. The kinetics of adsorption was investigated, and the adsorption found to very rapid for lead and cadmium and much slower for methylene blue. The contaminants could be desorbed, and the material recycled several times with the solid easily removed with a magnet.
Interaction of molecular oxygen with surface defects on single-particle organolead halide perovskites

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Organolead halide perovskites (OHP) have emerged as a promising material for applications in photovoltaics and optoelectronics. This new group of materials offers the simplicity of solution processing methods while having excellent optoelectronic properties. However, the commercial viability of the devices based on OHPs is still hindered by its poor stability, particularly, against ambient atmosphere (i.e. water and oxygen), prolonged exposure to high temperatures and high-intensity light. Recently, these deteriorating effects have been associated with the presence of chemical or physical defects in OHP bulk and surfaces. However, due to lack of direct measurement of their effects, the role of defects on the instability of OHPs are yet to be fully understood. In this report, we showed the influence of different gas environment on the ensemble time-dependent photoluminescence (PL) behavior of OHP nanoparticles. To gain mechanistic insights into the observed ensemble PL behavior, we did a detailed single-particle analysis of the individual OHP nanoparticles. In the end, we came up with a kinetic model to explain the observed phenomenon. In addition, using super-resolution localization microscopy, we were able to estimate the number and spatial distribution of surface defects on a single OHP particle.

COLL 212

Characterization of yellow-colored colloids in the Manasquan Watershed, NJ

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Discoloration and increased turbidity has been observed in the Manasquan watershed over the past years causing concerns about the quality of drinking water in Monmouth-Northern Ocean County, New Jersey. During the summer months, the water exhibits a strong yellow discoloration which cannot be removed by conventional treatment methods at the Manasquan Water Treatment Plant. The New Jersey Water Supply Association (NJWSA) has been working to resolve this issue by trying to identify the geologic/urban source of the yellow coloration in the Manasquan River. Despite continuing efforts by the NJSWA, the Manasquan River still goes through increased turbidity and color problems on a seasonal basis. In this investigation, we determined that the discoloration of Manasquan waters was caused suspended particulate matter. Water samples collected from Yellow Brook contained colored particles greater than 1 nanometer in size. The particles were stable as dispersed colloids in the water. Flocculation and settling of the particulate matter was not observed, even over the time scale of years. We conducted a proof-of-concept study to assess the feasibility of several state-of-the-art microscopic and spectroscopic techniques to characterize the...
physical and chemical form of the suspended particles in the Yellow Brook sample. We successfully obtained nanometer and molecular-scale information of the particles using dynamic light scattering (DLS), X-ray absorption spectroscopy (XAS), Scanning Transmission X-ray Microscopy (STXM), and Scanning Electron Microscopy (SEM).

COLL 213

Metal-assisted and microwave-accelerated germination

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We have developed a novel technique known as Metal-Assisted and Microwave-Accelerated Germination (MAMAG), that involves the combined use of gold nanoparticles and microwave heating to rapidly germinate seeds. We utilized a solid-state microwave (8 GHz, tunable power 20 W) with an applicator tip that has a 3 mm circumference and 4 mm penetration depth. Four-year-old basil seeds were placed in either deionized water or gold nanoparticles (Au NPs) (20 nm or 200 nm) in a 96-well plate. Dry basil seeds were used for control seeds. All basil seeds were treated with continuous microwave heating (2 W, 10 W, 20 W) for up to 6 minutes. We used bright-field, fluorescent, and scanning electron microscopy to characterize basil seeds before and after microwave heating. Basil seed gum (mucilage) was also characterized by scanning electron microscopy after microwave heating. We also examined basil seed esterase activity to determine if microwave heating and nanoparticles impacted esterase activity. We found that Au NPs delayed growth in basil seeds planted hydroponically as well as those planted in a greenhouse. Basil seeds exposed to the MAMAG technique were comparable to basil seeds in water only. However, basil seeds exposed to the MAMAG technique died slower than basil seeds in water only. Therefore, utilizing the MAMAG technique, we can control the basil seed germination process as well as delay basil seed death.

COLL 214

Metal-assisted and microwave-accelerated decrystallization of pseudotophaceous aggregates in human joint models

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Gout is a common inflammatory arthritis disease caused by inefficient metabolism of purines and the buildup of monosodium urate crystals in joints. Current maintenance therapies include the use of anti-inflammatory drugs, corticosteroids, and xanthine
oxidase inhibitors with side effects. Metal-Assisted and Microwave-Accelerated Decrystallization (MAMAD) technique have been used as an efficient technique to decrystallize organic and inorganic crystals with gold nanoparticles (Au NPs) which act as “nanobullets when exposed to microwaves heating. In this study, the MAMAD technique was examined as a possible treatment aid for gout and used for the decrystallization of laboratory synthesized monosodium urate monohydrate based pseudo-tophi submerged in 20 nm Au NPs, encased in pseudo-bursa in three synthetic human joint models. Model 1 and model 2 were exposed (model 1: Closed joint, dehydration of pseudo-tophi after each MAMAD session and model 2: Open and closed joint, dehydration of pseudo-tophi after 7 MAMAD sessions.) to 7 MAMAD sessions (i.e., a session = 120 seconds at 5 W,) and model 3 exposed to 18 MAMAD sessions in a rotated closed synthetic joint, dehydration after every 3 MAMAD sessions (i.e., MWH on the right, top, and left sides). Percent mass reduction (PMR; i.e., decrystallization) evaluated after exposure to the MAMAD technique. Our results showed that the application of the MAMAD technique in model 1 pseudo-tophi had an average PMR of 8.30±0.56% (closed joint), model 2, pseudo-tophi had an average PMR of 11.5±1.82 % (closed joint) and 5.89±1.59 % (open joint) and model 3 (rotated closed joint) 8.00 ± 2.53%. Our results demonstrate how the MAMAD technique can be a potential alternative treatment for gout with further studies.

**COLL 215**

**Magnetism and luminescence property of Mn\(^{2+}\)-doped and Cu\(^+\) doped \((\text{CdSe})_{13}\) clusters**

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A lamellar-template pathway of \((\text{CdSe})_{13}\) and syntheses of its doped 2D materials have been reported as important formation routes for diluted magnetic semiconductors (DMS). Herein we illustrate the fundamental studies regarding an atom-precise control of doping Mn\(^{2+}\) and Cu\(^+\) into \((\text{CdSe})_{13}\) which transforms into 2D materials. The paramagnetic ions were introduced into the magic-sized nanoclusters via a colloidal synthesis or cation exchange methods after sequential purification processes. Structural characterizations were conducted via HRTEM as well as synchrotron-based X-ray diffraction and absorption techniques. Spintronic properties can be revealed via MCD, EPR, fluorescence spectroscopies as well as Magneto-optic Kerr effect (MOKE). Correlated photon-induced magnetic and spintronic studies are under investigation for potential DMS applications.
A formation pathway for (CdSe)_{13}-pair into 2D materials

**COLL 216**

Uncovering key nanoparticle/chemistry adsorption mechanisms relevant to shallow trench isolation (STI) and copper (Cu) chemical mechanical planarization (CMP) performance

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Chemical Mechanical Planarization (CMP) is an enabling process in the semiconductor industry used to achieve global planarization on integrated circuits, which has ultimately led to the extension of Moore’s Law. CMP is used to effectively remove bulk material while limiting the amount of defects during the polishing process; this can be achieved by finding the delicate balance between the chemical action of the nanoparticle/chemistry dispersion (slurry) and the mechanical force applied during the polishing process. As the feature sizes of devices continue to shrink, it is crucial to limit defect formation, such as micro-scratches, particle contamination, galvanic corrosion/pitting, and line dishing and erosion. Contributing factors to defectivity include film formation and the difference in surface energy at the interface of the polishing pad, slurry, and substrate. Minimizing this surface energy difference can be used to improve defectivity commonly observed in STI and Cu CMP. Additionally, monitoring changes in
the coefficient of friction (CoF) at the substrate interface can be correlated to changes in slurry chemistry (i.e. surface adsorption), which is directly related to modulation of scratch defectivity. This study probed the role of slurry chemistry on surface energy modulation on respective CMP substrates in terms of wettability, surface roughness, CoF, and substrate removal rate. Initial results show strong correlation between surface hydrophilicity/hydrophobicity and defect propagation. Additionally, the synergy between nanoparticle size and effective chemistry surface adsorption results in significant defect reduction on both oxide and metal substrates.

**COLL 217**

**Multi-point alignment of 6,5 carbon nanotubes on DNA origami substrates**

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Among the wide variety of types of carbon with potential technological applications, the one-dimensional form, carbon nanotubes (CNTs) have presented significant barriers to incorporation into commercial devices, primarily due to purity and alignment issues. While there is a virtual periodic table (diameter and helicity) of carbon nanotube types, the 6,5 form stands out as a semiconductor to be targeted for development. 6,5 CNT’s display a relatively high fluorescent quantum yield and, under certain synthesis conditions, 6,5’s are also majority products, making them the most likely form to find early commercial applications.

As part of a program seeking to leverage the one-dimensionality of CNTs, we are developing extended one-dimensional DNA based origami platforms for the localization of 6,5 carbon nanotubes, with the expectation of incorporating these tubes as components in systems constructed on origami substrates. We have chosen to approach CNT immobilization on origami via two routes well documented for the case of single origami, utilizing either DNA bridging or protein (Streptavidin) bridging to bind the CNTs to multiple well-defined locations on the substrate. While significant levels of agglomeration are not observed as products of the solution phase reaction of single origami tiles with CNTs, significant agglomeration is observed when either long or shortened 1D origami polymers are reacted with CNTs. This agglomeration is essentially due to cross linking of the extended origami structures to each other intermediated by the CNTs. This agglomeration presents significant barriers to single molecule characterization and thus to implementation of long origami substrates in optical circuits containing CNTs. In order to minimize agglomeration, interfacial assembly experiments have been performed. This approach has been found, through AFM characterization, to essentially eliminate the cross linking, or agglomeration, barrier to progress. It is anticipated that the sequential surface reactions presented here may provide a pathway to high resolution, high density experimentation on single 6,5 carbon nanotubes.

**COLL 218**
**Photo-degradation of organic contaminants using a novel nano-carbon / TiO$_2$ layer-by-layer composite**

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Titanium dioxide (TiO$_2$), a semiconductor, has been extensively used as a photocatalyst and has been shown to have great potential for use in water treatment due to its high activity, stability and low cost. The use of carbon nanomaterials to enhance the activity of TiO$_2$ photocatalysts has received recent attention and improved performance has been demonstrated in composite systems using carbon nanotubes, graphene oxide, and activated carbon. The following work investigates the catalytic performance of TiO$_2$/nanocarbon films formed using layer-by-layer (LbL) deposition. Composite films were formed on quartz surfaces using a simple dip-coating technique using highly functionalized carbon nanoparticles derived from glycerol and Degussa P25 titanium dioxide. This technique allows for the immobilization of carbon and TiO$_2$ nanoparticles, both of which are now easily accessible to contaminants. Composite films were analyzed to determine surface microstructure, growth, and stability using UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Film growth was found to be linear with the number of bi-layers deposited and the material showed good catalytic activity for the degradation of methylene blue at 365nm. Photocatalytic activity as a function of layer composite thickness and the light wavelength was also investigated. The Carbon / TiO$_2$ LbL system was used to test the photo-degradation of various organic compounds and the reusability of the films was demonstrated.

**COLL 219**

**Predicting size dependence of CdSe quantum dot net charge using modified charge equilibration methods**

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Colloidal dispersions of nanoparticles are known to have permanent net-dipoles and net-charges. The charge properties of quantum dots have been demonstrated to be solvent dependent and are typically observed in apolar solvents. Particularly, CdSe quantum dots in colloidal dispersions can take on an overall net-charge in solution as a result of thermal charging. The net-charges on quantum dots due to thermal charging open up a range of possibilities for manipulating the nanocrystals into larger heterostructures or electrophoretic deposition onto substrates for use in photovoltaics. Charge equilibration was modified to reflect the physical environment of colloidal quantum dots, which is approximately: a sphere with a dielectric constant differing from that of the surrounding medium, typically a stabilizing ligand such as trioctyl phosphine oxide (TOPO). The mismatch between the dielectric properties of the quantum dot and the surrounding medium screens the interactions between charges in a manner dependent
on position relative to the surface of the quantum dot. This modified charge equilibration method was applied to CdSe quantum dot structures in the radial range: \(1 \text{Å} \leq R \leq 12.5 \text{Å}\). The total charge constraint in charge equilibration was varied from -10 to 10 for each structure. A minimum energy (eV/pair) for each quantum dot was determined at some charge between -10 and 10. The particular net-charge that afforded the minimum energy for the quantum dots was found to be strongly size dependent. Specifically, as quantum dot radius increased, the net-charges that resulted in greatest energetic stability, when imparted on quantum dot structures of similar radii, became increasingly positive. In other words, the CdSe quantum dot net-charge is size-dependent.

**COLL 220**

**Metal-assisted and microwave-accelerated treatment and prevention of bacterial infections**

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Antibiotics have traditionally been effective in killing bacteria and treating infections, but certain bacteria show resistance to these treatments making infections more difficult. The Aslan Research Group has developed a novel technique, the Metal-Assisted and Microwave-Accelerated Treatment and Prevention (MAMATP), which uses a combination of gold nanoparticles (AuNPs) and medical microwaves to disrupt foreign substances on the skin. Selective heating is activated, and a temperature gradient is created between the AuNPs and the solution in which they are contained. The kinetic energy of the AuNPs increases, resulting in “nano-bullet” collisions between the AuNPs and the bacteria on the surface. To simulate bacterial infection, we have used polystyrene microspheres as a model bacterial colony. We applied our MAMATP technique using 20, and 200 nm AuNPs, 10 and 100 um microspheres, microwave heated at powers of 2, 10, and 20 W, with 2 minutes of heating/cooling cycles for a total of 20 mins of heating. We observed, organization, micelle formation, and destruction of these microspheres using MAMATP technology as evidenced by scanning electron microscopy. Upon complete characterization of the microspheres we will convert this technique to a combination of AuNPs and microwaves for effective antibacterial treatment and prevent recurrence of bacterial growth on skin.

**COLL 221**

**Semiconducting Langmuir-Blodgett films of copper paddle-wheel frameworks**

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Porphyridin containing structures are desirable for their light harvesting abilities and their potential for various photocatalytic applications. However, the use of porphyrin-based materials in devices is limited by the aggregation of the porphyrin rings. Ordering the molecules into a uniform, crystalline structure of a porphyrin-containing metal-organic framework (PMOF) increases the efficiency of the material and allows for permanent porosity.

We studied two paddle-wheel porphyrin framework (PPF) thin films consisting of porphyrin ligands connected with copper clusters. The films were formed at the air-liquid interface via the Langmuir-Blodgett method. The two films contain the same organic porphyrin ligand and Cu linker, but one consists of a copper ion coordinated in the center of each porphyrin ligand (Cu-PPF-1) and the other does not (Cu-PPF-2). This study focuses on measuring the junction current of the Cu-PPF materials and exploring the charge transfer behaviors along the horizontal and vertical directions. Based on the coordination of a Cu-ion in the porphyrin center, the charge carrier movements can be induced by either metal-metal interactions or through metal-ligand transfer. We used a hanging drop mercury electrode (HDME) and a thin film electrode system to study the electron transfer through the films vertically and horizontally. Cu-PPF-1 was shown to have a slightly higher current density than Cu-PPF-2 along the vertical direction. This increase in current density was possibly due to the metal ion doped in the center of the porphyrin ring, promoting a superexchange electron transfer process. Study of the electron transfer of PMOFs will promote the fundamental understanding of photocurrent production by these materials, which will benefit the development of light harvesting devices.

COLL 222

Effects of stabilizing ligands on nanoparticle sintering during calcination in supported nanoparticle catalysts

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Traditional supported nanoparticle synthesis methods require the use of stabilizing ligands to passivate the nanoparticle surface to protect from nanoparticle growth and agglomeration. These ligands often deactivate the catalyst by blocking metallic active sites. Thus, stabilizing ligands typically must be removed prior to use most commonly through a high-temperature annealing step. In traditional systems, it is reported that exposure of nanoparticles to high temperatures causes significant and uncontrollable nanoparticle growth, however; the fundamental causes for this growth have not been investigated. In a previous work, we showed that ligand-free, supported nanoparticles grew significantly less during calcination than those prepared via traditional methods. In this work, we demonstrate that nanoparticle growth during calcination in traditionally-prepared, supported nanoparticle catalysts is a result of weakened nanoparticle-support attractive forces caused by the presence of the stabilizing ligand that separates the nanoparticle from the support material. Here, silica gel support material was
functionalized with triethoxysilane monolayers of varying thicknesses. Ligand-free nanoparticles were then deposited on top of the monolayers by utilizing a switchable surfactant system in which the stabilizing ligand is easily removed from the nanoparticle surface during deposition. The supported nanoparticles were then calcined and imaged with transmission electron microscopy. Image analysis shows that the nanoparticles separated from the support by the thickest monolayer grew significantly more during calcination than those separated from the support by a shorter distance. These results demonstrate that nanoparticle growth during calcination in traditionally prepared supported nanoparticle catalysts is a result of weakened nanoparticle-support interactions caused by the presence of stabilizing ligands on the metallic surface.

**COLL 223**

**Time-resolved temperature measurements of gold nanorods on surfaces in different media**

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We use a new time-resolved temperature measurement technique to measure the temperature from gold nanorods on a surface with a thin AlGaN:Er layer immersed in air, water and ionic solutions. This technique relies on temperature-jump luminescence thermometry using time-resolved peak intensity changes from Erbium ions embedded in the AlGaN layer. Temperature is calculated by measuring the relative peak areas of the $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ bands from Er$^{3+}$ ions using Boltzmann statistics. Finally, we compare our temperature-jump results to simulated thermal transfer data generated using finite element methods.

**COLL 224**

**Patterned perovskite thin film and single microcrystal arrays on a chemically patterned flat substrate**

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Perovskites have stimulated the interest of scientists and engineers who are eager to study and rationalize its fascinating photochemical properties. Their findings resulted in the development of solar cells, photodetectors, and light emitting diodes among many other devices. Compared to other materials, perovskite exhibits long carrier lifetime, long carrier diffusion length and high carrier mobility upon exposure to light. Recent progress in patterning perovskite materials involve the use of templates, such as packed microspheres, and porous membranes, which brought about solar cells with better efficiencies and photodetector arrays used for imaging. Other groups employed
stamps or molds to imprint the pattern as the perovskite crystallizes out of the precursor solution. A more direct approach was also adapted by some groups by using a laser or focused-ion beam to generate patterns either by evaporating the precursor solvent or by etching. Another approach, which is the focus of this research, is to deposit or grow perovskite films or crystals on a chemically patterned surface. While other groups used structurally patterned substrate to control the adsorption of the precursor, our group used a flat substrate with chemically patterned wettability to spatially control the adsorption of the perovskite precursor solution.

Under the right experimental conditions, we show that it is feasible to fabricate patterned perovskite thin films and grow an array of single perovskite microcrystals on a chemically patterned surface generated through a simple two step photoinitiated thiol-ene coupling reactions on a vinyl-functionalized substrate. These patterned perovskite films and microcrystal arrays can be developed into LED or photodetector arrays.

**COLL 225**

2D nanosheets with binding multivalency for the optical detection of pathogenic bacteria

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Two dimensional (2D) transition metal dichalcogenides (TMDs) have received considerable attention due to their unique optical characteristics. To exploit the TMD nanosheets as biosensors, it is necessary to exfoliate and functionalize TMDs in an aqueous solution. Herein, we report an effective approach to the simultaneous exfoliation and functionalization of TMD nanosheets with a biocompatible polymer, dextran, in water. The strong multivalent hydrogen bonding ($\Delta E_b = -0.52$ eV) between the hydroxyl groups of dextran and the chalcogenides of the TMD nanosheets enabled to effectively exfoliate and functionalize TMD monolayers in water, resulting in TMD/dextran hybrids (dex-TMDs). The resulting dex-TMDs exhibited a stronger affinity to *Escherichia coli* O157:H7 than *E. coli*-specific antibodies and aptamers. In addition, the dex-TMDs were able to selectively detect a single copy of *Escherichia coli* O157:H7 without the use of antibodies. Similarly, dex-TMD can identify *Escherichia coli* O157:H7 specifically without using antibodies. This new biosensing principle can be expanded to detect a variety of biological molecules.

**COLL 226**

Metal-ligand self-assembly on powdered supports: A novel strategy towards heterogeneous single-site catalysts

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High levels of reaction selectivity for heterogeneous catalysis are generally difficult to achieve with traditional metal nanoparticle catalysts, due to the variety of metal binding sites available. Motivated by the desire towards uniform reaction sites, there is growing interest in developing single-site catalysts (SSCs). Our group approaches this challenge using redox self-assembly of metal-organic systems at surfaces. Our previous work has demonstrated the formation of metal single-sites on single crystal surfaces in UHV by co-depositing metals (Pt, V, Cr, or Fe) and oxidizing ligands with suitable binding pockets (JACS 2014, 136, 9862; JCP 2015, 142, 101913; JACS 2015, 137, 7898; JPCC 2017, 121, 13183; Chem. Sci. 2018, 9, 1674). A uniform chemical character of the metal cations is controlled by the coordinating ligands. Here, we present the application of this self-assembly strategy on high-surface-area powdered oxide supports. Simultaneous wet impregnation of metal precursors and well-designed ligands creates oxide-supported metal-ligand SSCs (J. Catal. 2018, 365, 303). Structures of resulting SSCs are elucidated by a wide range of characterization techniques, including XAS, XPS, TEM, XRD, and CO adsorption DRIFTS. This synthesis strategy has been successful with multiple metals (Pt, Ir, and Rh), ligands, and supports (MgO, CeO₂, Al₂O₃, and TiO₂); however, we have also discovered limitations in its scope, which we interpret in the context of competing metal-ligand-support interactions. We have shown successful catalysis with our metal-ligand SSCs in various reactions, ranging from alkene hydrosilylation in a solution-phase batch reactor to hydrogenation reactions in a gas-phase flow reactor. Catalytic results from these reactions highlight several advantages of SSCs over traditional metal nanoparticle catalysts, including metal dispersion, higher selectivity, and improved durability.

COLL 227

Assembling gold nanorods using secondary structure transitions in electrostatically adsorbed poly-l-lysine

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The class of nanomaterials that support surface plasmon resonance, namely gold and silver nanoparticles, are of particular interest due to their unique optical properties. While isolated nanoparticles are useful as sensors, patterned and organized plasmonic structures can have significantly higher sensitivities. It is possible to fabricate plasmonic arrays with features tailored to maximize the enhanced electromagnetic fields using traditional top-down lithographic methods. However, these top-down methods require extensive instrumentation as well as a dedicated facility for fabrication. In contrast to the traditional top-down lithographic fabrication methods, we are exploring bottom-up solution phase assembly methods. Our work focuses on the reversible assembly of gold nanorods in solution using a pH dependent transition in the secondary structure of poly-l-lysine (PLL). In this work, CTAB capped gold nanorods are first coated with a negatively charged polyelectrolyte (polystyrenesulfonate, polyaspartate, or polyacrylate) followed by the positively charged PLL using standard Layer-by-Layer deposition. The
secondary structure of the PLL can be tailored by changing the pH of the solution. Below the pKa, random coil and β-turn structures dominate and as the pH is raised above the pKa, the amine moieties of the lysine residues are deprotonated and the secondary structure switches from random coil to predominantly α-helical and antiparallel β-sheet conformations. The secondary structural changes that occur when the solution pH > pKa results in assembly of the PLL coated gold nanorods. Additionally, CD spectroscopy gives deeper levels of insight in that we can simultaneously measure the molecular (UV region) and the suprastructure (Vis-NIR) chirality due to the well-resolved CD signals.

COLL 228

Emulsions stabilized by chemically heterogeneous nanoparticles

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Nanoparticles chemically modified to be surface-active can adsorb strongly at the oil-water interface to stabilize emulsions. However, few studies of the effect of chemical heterogeneity on nanoparticle adsorption at the oil-water interface have been reported. Recent studies have revealed the importance of nanoscale chemical heterogeneity on the interactions between hydrophobic groups in water, with diverging effects observed when cationic groups are proximally located (< 1 nm) to a nonpolar domain. Since hydrophobic interactions provide a driving force for oil-water emulsification, elucidating these effects in the context of chemically heterogeneous nanoparticles is important for the control of nanoparticle assembly at the oil-water interface. We will describe an investigation of the effect of different polar functional groups displayed by chemically heterogeneous nanoparticles on their adsorption behavior at the oil-water interface to stabilize emulsions. Our approach is based on the use of gold nanoparticles functionalized with binary mixtures of alkanethiols displaying nonpolar and polar (both charged and uncharged) functional groups as a model system. Oil-water emulsion stability for the different nanoparticle surface chemistries is assessed by characterizing differences in oil droplet sizes using optical microscopy and dynamic light scattering methods. The effect of the nature and charge of the polar groups displayed on the nanoparticle surface, as well as the effect of nanoparticle surface composition (ratio of polar to nonpolar groups) on interfacial activity of the functionalized nanoparticles and resulting emulsion stability will be discussed.

COLL 229

Anion exchange and extinction coefficient determination of cesium lead halide nanocubes

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Metal halide perovskites are new materials of interest in the field of nanoscience due to the increased efficiency of solar cells containing them. Our work surrounds the synthesis of cesium lead bromide (CsPbBr$_3$), subsequent halide exchanges to cesium lead chloride and iodide, and molar extinction coefficient calculations for the bromide and iodide species. By varying ratios of chloride and iodide ions in solution, homogeneous nanocrystals were created that were mixtures of the original parent compounds and the emission spectra showed maxima across the entire spectral region. The optical properties of all CsPbX$_3$ (X = Cl, Br, I) nanocrystals were characterized by absorbance and fluorescence spectroscopy, and crystal structure and size were determined by x-ray powder diffraction and transmission electron microscopy. The concentration of cations in the samples were determined using induced coupled plasma optical emission spectroscopy (ICP-OES). Using spectroscopy and mathematical modeling the extinction coefficients for the bromide and iodide species were determined. Knowledge of the extinction coefficients is imperative for further studies on these materials, as precise concentrations are known.

**COLL 230**

**CTAB-controlled silica coating on nanorods and its impact on surface plasmon resonance**

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Silica coated gold nanorods (SiAuNRs) have shown tremendous utility in the fields of nanotechnology and biology due to their biocompatibility and enhanced thermal, mechanical, and colloidal stability. In this work, we have focused on studying the cationic bromide (CTAB) controlled silica coating on AuNRs and its impact on surface Plasmonic resonance (SPR). The CTAB-coated AuNRs were prepared based on the popular seed-mediated method followed by tetraethylorthosilicate (TEOS) polymerization leading to the formation of silica layer coated on the surface of AuNRs. Our results show that the changes of shell thickness is in agreement with the SPR shift. The morphology of silica shell is altered from a uniform thickness layer to a dumb-bell-like shape by controlling CTAB amount. We have proposed a model of CTAB controlled silica coating in order to understand the results.

**COLL 231**

**Towards tunable nanostructures using electroactive amphiphiles**

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Poly(aniline), PANI, is a well-known conducting polymer owing to its ease of synthesis, attractive optoelectronic properties, and its existence in multiple oxidation states. Its low solubility, polydispersity and poor processability make it a complex system to study and
explore. Therefore, oligo(aniline)s are attractive as an ideal replacement, as the oligomers have the same desirable redox properties and tunable chemical structure as PANI, as well as good solubility and processability. Amiphiles based on tetra(aniline), the shortest oligo(aniline), are a class of molecules which have recently attracted interest owing to their self-assembling behaviour in aqueous environments. A single-tailed ammonium amphiphile EB Ph/NH₂ TANI-C₆NMMe₃Br⁻ (TANI-PTAB) has been prepared in our group, and exhibited the formation of self-assembled wire-like nanostructures. More recently, we proposed a fascinating strategy to tune the self-assembled structures of TANI-PTAB reversibly between wire and vesicle-like structures using the role of the packing parameter. To further explore the behaviour of the family of TANI-based amphiphiles, a TANI-based phosphonium amphiphile (i.e., TANI functionalised with alkyltrimethylphosphonium head group) was designed for comparison with TANI-PTAB. Successful synthesis of the electroactive amphiphile EB Ph/NH₂ TANI-(C₆PMe₃Br₂) (TANI-PTPB) was confirmed using different characterization techniques including 'H and 'C NMR spectroscopy and accurate mass spectrometry. Results from investigations into the formation of self-assembled structures, and their tunability and addressability will be presented.

COLL 232

Surface alignment transitions in liquid crystals induced by exposure to formaldehyde gas

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We report the development of formaldehyde gas sensors based on surface-driven alignment transitions in films of liquid crystals (LC). Formaldehyde is an indoor pollutant that is emitted from building materials, including glues, fiberboard, plywood, and paints. Despite its prevalence, formaldehyde is a known carcinogen and OSHA stipulates that the permissible exposure limit for formaldehyde should not exceed 0.75 parts per million (ppm) in air measured as an 8-hour time-weighted average. We developed novel interfaces for detection of formaldehyde consisting of films of LC mixtures supported on a metal surface. The LC mixtures consisted of nitrile-containing aromatic compounds, and a ketone-containing aromatic compound. The alignment of the LC molecules at the interface with the metal surface, and thus the optical properties of the LC films, was found to depend on the composition of the LC mixtures and the identity of the supporting surface. LC mixtures containing >2 vol.% of the ketone-containing aromatic compound exhibited alignment perpendicular to the surface (homeotropic) when supported on gold, appearing dark when observed with cross-polarized light. Upon exposure to formaldehyde, these LC mixtures exhibited an optical transition from dark to bright, consistent with a change in surface orientation from homeotropic to planar (parallel to the surface). Using a mixture containing 3 vol.% of the ketone-containing compound, we observed an optical response in the LC films at 0.75 ppm of formaldehyde, which is the concentration relevant for monitoring human exposure. We hypothesize that the observed formaldehyde-induced optical response is a
consequence of competitive adsorption at the gold surface between formaldehyde and
the ketone-containing compound in the LC mixture. These studies provide fundamental
insights on the bonding and orientation of molecules at solid interfaces that could give
rise to the development of new functional LC materials.

COLL 233

Exploiting directed assembly to obtain precise coupling between colloidal silica
whispering gallery mode resonators

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Microspheres are very attractive candidates for whispering gallery mode (WGM)
resonators due to their ease of fabrication, strong optical confinement, ultrahigh quality
factors, and low mode volumes. A very interesting and unique feature about whispering
gallery mode resonators is the evanescent field that arises just outside the cavity,
extending hundreds of nanometers outside of the circumference. Small perturbations of
this evanescent field can be easily detected, enabling ultra-sensitive label free WGM
detectors. Additionally, interesting coupling phenomena can be observed and exploited
by taking advantage of the evanescent. It is well understood and very important to note
that the strength of the evanescent field decays exponentially as the distance from the
cavity edge increases. Generally, coupling of WGM resonators is afforded via e-beam
lithography or via precise positioning of incident probes, offering little to no tunability.
This work puts a spin on an old technique, directed assembly of colloids, to achieve
strong WGM resonator coupling. By taking advantage of 3-D lithography and directed
assembly, unique coupling geometries can be observed, resulting in interesting optical
properties, including enhanced photoluminescence.

COLL 234

Partial molar volumes and volume of mixing of salts and osmolytes

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Solute-solvent interactions were studied by volumetric analysis for a series of salts and
osmolytes. Densities of anion and cation salts from the Hofmeister series and seven
osmolytes at varied concentrations were measured to determine the apparent molar
volume of the solute, partial molar volume of solvent and solute, and volume of mixing
in aqueous solutions. Strongly hydrated salts showed smaller limiting partial molar
volume compared to weakly hydrated salts. Volume of mixing values were more
negative for strongly hydrated anions and cations suggesting that the interactions of
these salts with water were more favorable. The interactions between osmolytes and water were also investigated in a similar fashion as the slats. Detailed volumetric analysis of solute-water system will be presented.

**COLL 235**

**Size control on zeolitic imidazolate framework-8 particles for gas sensing**

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Zeolitic imidazolate framework-8 (ZIF-8), a type of metal-organic framework (MOF), is composed of tetrahedral zinc ions connected with 2-methylimidazole ligands forming a sodalite structure. ZIF-8 has demonstrated great potential in gas sensing due to its intrinsic characteristics of large surface area and porosity. In an endeavor to improve upon this quality, we successfully synthesized ZIF-8 particles with a controlled size ranging from 100 nm to 10 μm in diameter. Two distinct methods of synthesis were utilized. First, by modulating the ratio between zinc nitrate hexahydrate and 2-methylimidazazole, we were able to vary the ZIF-8 particle size in nanoscale. Second, switching synthesis solvent from methanol to dimethylformamide promoted particle growth in the microscale range. The chemical composition, crystal structures, and porous properties of the produced ZIF-8 particles were analyzed using infrared spectroscopy, X-ray diffraction, and nitrogen gas sorption analysis, respectively. Additionally, scanning electron microscope (SEM) studies confirmed that uniform particles were produced with diameters of 100nm, 300nm, 400nm, and 10μm, respectively. Interestingly, atomic force microscope (AFM) imaging studies revealed that the three larger particles were in fact aggregations of 100nm particles. To address this, a surfactant assisted synthesis study was conducted. (1-Hexadecyl)trimethylammonium bromide was introduced to the synthesis process in an effort to reduce surface tension and promote crystal growth. Analysis of surfactant assisted synthesized ZIF-8 particles will promote the fundamental understanding of the heterogeneous crystal growth with the effect of a electrical double layer (EDL).

**COLL 236**

**Shiga and cholera toxins induce roll-up of membranes**

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Many types of membrane interacting proteins induce spontaneous curvature upon membrane binding. Shiga and Cholera toxin both belong to the AB5 family of toxins and both consist of a toxic (active) A subunit and a membrane-binding pentameric B subunit.
It is known that Shiga and Cholera toxin induce tubular membrane invaginations in GUVs due to curvature effects. This is modeling endocytosis of the toxin through the plasma membrane of cells.

We have recently studied Annexins which is another class of curvature-inducing proteins. Annexins have important functions in plasma membrane repair where curvature near hole edges is a key event in the repair process.

As a model system to characterize curvature-inducing proteins, we study the morphology induced in planar membrane patches. It was previously shown that Annexins induce characteristic morphologies in membrane patches including membrane rolling.

In this study we show that the B subunits of Shiga and of Cholera toxin (StxB, CtxB) both induce roll-up of cell-sized membrane patches. Rolling starts from the free membrane edges of the patch and is completed within a few seconds. We quantify the rolling speed and morphology of rolls induced by the toxins. Our results indicate that membrane rolling may be a general effect displayed by many proteins that induce negative curvature.

**COLL 237**

**Self-assembly of surfactants at air-liquid interfaces**

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Quaternary ammonium salts (surfactants) are widely used as corrosion inhibitors to protect the oil and gas transportation pipelines from internal corrosion. The tail length plays a vital role in corrosion prevention of metal surfaces. The inhibition property of surfactants is limited by various operating conditions such as temperature, flow rate, dissolved salt concentration in crude oil, and the nature of the metal surface. This research focuses on understanding the correlation between adsorption and molecular organization of surfactant molecules at the air-liquid interface using sum frequency generation (SFG) spectroscopy. The conformational changes undergone by the selected surfactants were investigated at SSP and PPP polarizations by varying the alkyl tail length from butyl (C4), hexyl (C6), octyl (C8), decyl (C10), and dodecyl (C12). 8.0 mM solutions in water were prepared for five Quat compounds. The spectral profiles from shorter tail lengths (butyl and hexyl) differ from longer ones. Poorly oriented OH (~3200 cm\(^{-1}\)-3600 cm\(^{-1}\)) region for butyl and broader OH region were observed for hexyl surfactants compared to others. These surfactants were also investigated with 0%, 0.5%, 1%, 5% and 10% (wt%) NaCl at air-liquid interfaces. The SF intensities of OH region decrease at both SSP and PPP polarizations with increasing salt concentrations or ionic strengths. This is associated with the screening effect which reduces the number of water molecules at double layer region. In PPP polarization, the OH region shifted toward ‘water-like’ structure (~3400 cm\(^{-1}\)) of water from ‘ice-like’ structure (~3200 cm\(^{-1}\)) of water due to disturbing the order of the interfacial water by adding salts. The CH region of C4 tail length resulted to a more ordered monolayer from 0% to 10% NaCl gradually. The CH region of hexyl C6 tail length was barely visible at 10% NaCl. The tail lengths and salt concentrations significantly affected the organization of interfacial molecules.

**COLL 238**

**End-group functionalized polymer ligands for QD-based luminescent solar concentrators**

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Luminescent solar concentrators (LSCs) enhance the efficiency of photovoltaic devices (PVs) through the absorption and redirection of light by nanocrystal quantum dots (QDs) in a polymer matrix. This research is aimed at producing a finely tuned polymer matrix for use in luminescent solar concentrators to control the dispersity and aggregation of nanocrystal QDs. Through an exchange of native ligands for selected telechelic polymers, nanocrystal QDs are functionalized with poly(methyl methacrylate) (PMMA) ligands of known chain length. Prior to ligand exchange, polymers of targeted molecular weights (1-10 kDa) are synthesized by living polymerization of methyl methacrylate to adjust the ligand properties on the QD. The homogeneity of these polymer coated QDs
in polymeric LSCs is described and the optical properties of the LSCs are related to the extent of QD dispersion.

Native ligand QDs in an LSC

Polymer coated QDs in an LSC

**COLL 239**

**Improving the functionality of carbon dots via doping and functionalization**

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Carbon dots are a class of carbon nanomaterials that exhibit unique properties such as multicolor emissions, photostability, low toxicity, and biocompatibility. These unique properties have enabled a wide range of applications ranging from cell imaging to photothermal therapy and photovoltaic applications. However, their properties and functionality still need to be improved in many aspects. One way of doing this is through doping and surface functionalization. Doping tunes the electronic properties of carbon dots while functionalization creates or changes surface states, thus influencing their solubility and applications. Here in, we demonstrate the tuning of electronic and optical properties of carbon dots via doping/co-doping with various atoms like B, N, and S etc. The functionality is demonstrated by modifying the surface of the carbon dots with different groups such as amine and carboxylic acid groups. Characterization will be performed through various techniques including X-ray Photoelectron Spectroscopy.
(surface groups), Dynamic Light Scattering Spectroscopy (particle sizing), Transmission Electron Microscopy (particle size and morphology), UV-Vis Spectroscopy and Fluorescence Spectrophotometry (optical properties).

**COLL 240**

Deuterium NMR spectroscopy in colloid and surface chemistry

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Solid-state deuterium NMR spectroscopy is a powerful method for addressing how material properties emerge from atomic level interactions in the case of surfactants and lipid membranes. We show how solid-state ²H NMR gives atomistically resolved structure and dynamics of flexible phospholipids within the liquid-crystalline state. For lamellar mesophases, the average structure is manifested by the segmental order parameters \( S_{CD} \) of the molecules. Bilayer deformation in response to external perturbations allows one to unravel how the bulk material properties emerge from atomistic-level interactions. Moreover, the extent to which lipid bilayers are deformed by osmotic pressure is integral to how lipid-protein interactions affect membrane functions. Measurements of the order parameters versus osmotic pressure yield the elastic area compressibility modulus and the corresponding bilayer thickness at an atomistic level. Notably, this approach reveals that membrane elasticity involves bilayer deformations over a range of length scales, from the nanostructure dimensions down to the size of the flexible lipid segments. In addition, NMR relaxation rates provide complementary information about molecular dynamics. Particular attention is paid to the magnetic field dependence of the NMR relaxation rates in terms of various simplified power laws. We show how analytical NMR relaxation models can guide the continued development of atomistic and coarse-grained force fields. Our interpretation suggests that lipid diffusion and collective order fluctuations are implicitly governed by the viscoelastic nature of the liquid-crystalline ensemble. Collective bilayer excitations are emergent over mesoscopic length scales that fall between the molecular and nanoscale dimensions, and are important for lipid organization and lipid-protein interactions. Future conceptual advances and theoretical reductions will foster understanding of biomembrane structural dynamics through a synergy of NMR measurements and molecular simulations.

**COLL 241**

Quasielastic and elastic neutron scattering of membrane proteins

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Conventional X-ray crystallography has played a prominent role in our understanding of membrane protein structure, yet there are major gaps in understanding the dynamical basis for their functional mechanisms. Rhodopsin is the visual receptor and is an important prototype for membrane proteins of the G-protein-coupled receptor (GPCR) class. We hypothesized that light absorption by rhodopsin leads to an influx of bulk water into the protein core that regulates the catalytic binding and unbinding of the cognate G-protein, transducin. By combining small-angle neutron scattering (SANS) and quasielastic-neutron scattering (QENS) we investigated how the bulk solvent and the hydration shell govern structural fluctuations during rhodopsin activation. In SANS experiments rhodopsin was solubilized in CHAPS or DDM detergents, and data were collected under detergent-contrast matched conditions to isolate the protein structural changes upon photoactivation. The QENS experiments compared the β-fluctuations that are coupled to the hydration shell of the ligand-free opsin versus the dark-state rhodopsin in partially hydrated ($h=0.27$) powdered protein samples. We discovered how the rhodopsin fluctuations are slaved to bulk water and the hydration shell. In the fully hydrated state, the α-fluctuations are coupled to the bulk solvent, opening up the protein structure and facilitating activation of the G-protein transducin. We discovered that local hydrogen-atom dynamics in the light-activated state are on-average slower, indicating greater steric crowding versus the dark-state rhodopsin. Our experiments suggest that the light-activated state of rhodopsin is swollen yet locally more compact as a result of increased interactions between the hydrophobic groups to accommodate the penetration of water into the protein core. Integrating SANS for the fully hydrated protein with QENS for the partially hydrated protein reveals unprecedented insights into the energy landscape of the GPCR activation process.

**COLL 242**

**Flexible surface model for lipid-protein interactions**

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Membrane protein conformational changes—involving folding, stability, and membrane shape transitions—potentially involve elastic remodeling of the lipid bilayer. Evidence
suggests that membrane lipids affect proteins through relatively long-range interactions, extending beyond a single annulus of next-neighbor boundary lipids. Application of the theory of elasticity, derived from classical physics, explains the polymorphism of both detergents and membrane phospholipids. A flexible surface model (FSM) describes the balance of curvature and hydrophobic forces in lipid-protein interactions. Chemically nonspecific properties of the lipid bilayer modulate conformational energetics of membrane proteins. The new biomembrane model challenges the standard fluid mosaic model found in biochemistry texts. Influences of bilayer thickness, nonlamellar-forming lipids, detergents, and osmotic stress are all explained by the FSM. According to the FSM, geometrical deformation of the lipids adjacent to the protein to match the spontaneous (intrinsic) monolayer curvature counterbalances the unfavorable hydrophobic mismatch. Membrane curvature elasticity and concepts of a flexible surface and minimal surfaces were formulated by Helfrich and have found widespread application in the field of surfactant and membrane nanotechnology. Similar concepts are applicable to biomembranes, where membrane stress fields govern energetics of protein conformations due to their different shapes within the bilayer. As an example, rhodopsin activation is known to be promoted by nonlamellar-forming lipids characterized by small headgroups and polyunsaturated acyl chains. Upon light absorption, rhodopsin becomes a sensor of the negative spontaneous curvature of the membrane. If the monolayer tends to curve towards water, then an elastic two-way coupling of the protein to local monolayer curvature can occur. Increased awareness of curvature forces closely links structural biology to lipid physical chemistry to explain biomembrane structure and function.

**COLL 243**

**CdSe quantum shells growth on CdS core nanocrystals**

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Nanocrystal are small crystalline particles that are only several nanometers in size. Quantum dots are semiconductor nanoparticles that have unique size-dependent optical and electric properties due to the phenomena called quantum confinement; used for various devices such as LEDs, biomedical dyes, and solar cells. However, their small size was problematic due to a higher chance of an electron getting trapped between a layer of quantum dots. As a solution, we grew a quantum layer of semiconductor material over a large core nanocrystal, to retain its unique properties. Using colloidal synthesis, Cadmium Sulfide (CdS) was grown past quantum confinement and, using the same method, Cadmium Selenide (CdSe) shell was grown over the large CdS. Once we had CdS/CdSe core/shell nanocomposites, it was made into a thin film to test the photocurrent. To confirm the growth and size of CdS past quantum confinement, the absorption of the nanoparticles and the transmission electron microscopy (TEM) image was taken. Conductivity was determined for a 4.5nm CdSe, 17 nm CdSe, and 18nm CdS/ CdSe shell. The conductivity of the CdS/ CdSe shells was the largest in comparison to a 4.5 CdSe and 17nm CdSe.
Designing glycocalyx-mimetic interfaces for blood-contacting biomaterials: New insights from single-molecule microscopy

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Understanding of nonspecific protein adsorption mechanisms at solid-liquid interfaces is critical to rational design of surfaces for biomedical and industrial applications, such as medical devices, drug delivery carriers, marine coating, and biosensors. For blood-contacting medical devices, for example, contact with blood results in rapid nonspecific protein adsorption. This protein layer may initiate blood clotting by promoting platelet adhesion, activation, and aggregation. Therefore, materials are often engineered to enhance resistance to nonspecific protein adsorption through surface modification. Optimizing the design of blood compatible surfaces requires a detailed understanding of protein-surface interactions.

Protein interaction with solid interfaces is a result of transport, adsorption, desorption, and reaction processes. Individual protein surface interactions can result in reversible or irreversible binding, and some proteins may also undergo conformational changes after adsorption.

We have developed glycocalyx-like surface coatings, by combining layer by layer assembly of polyelectrolyte multilayers (PEMs) with GAG-rich polyelectrolyte complex nanoparticles (PCNs) at specific solution pH and salt concentration to study the mechanical properties and protein-surface interactions in detail, on a controlled model surface. We have used single-molecule tracking to measure a large number of single protein trajectories (>10⁴ in each experiment) to explicitly visualize the processes of adsorption and desorption of albumin and fibrinogen on these model surfaces. These direct experimental observations inform a mathematical model that describes protein adsorption and desorption and possible denaturation. This detailed characterization of protein-surface interactions can be used to design improved glycocalyx mimetic surfaces for blood-contacting biomaterials.
Coll 245

Synthesis and characterization of Gd:InP/ZnS quantum dots for an MRI-active Parkinson's disease probe

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Quantum dots (QDs), which are intensely fluorescent nanocrystals ranging 2-10 nanometers in diameter, have shown promise in fluorescence imaging. However, in vivo applications of QDs are limited due to the opaque surrounding of tissue and bones. In this study, InP/ZnS QDs were doped with a paramagnetic atom in an attempt to render them MRI-active. We have further bioconjugated these nanoprobes to develop highly specific MRI-active probes that can be used for detection of neurodegenerative
diseases. These bioconjugated nanoprobes detect a mutated form of alpha-synuclein that forms oligomers that are a hallmark of Parkinson’s disease and other alpha-synucleinopathies. Here, we have optimized the doping of QDs with MRI-active metals (e.g., Gadolinium and Manganese) and characterized the MRI activity. The resulting nanocrystals were further studied to assess the success of the paramagnetic atom’s incorporation into the crystal lattice and its performance as a probe for alpha-synucleinopathies such as Parkinson’s disease.

COLL 246

Adsorption of water-soluble peptoids to synthetic phospholipid membranes monitored by Second Harmonic Generation (SHG)

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Peptoids (N-substituted oligomers) are peptidomimetic molecules that are resistant to protease degradation and have increased biostability and membrane permeability. Peptoids have exhibited therapeutic and antibacterial properties. To develop peptoid-based therapeutics and antibacterial coatings, we need an increased understanding of their interactions with cell membranes. Adsorption of water-soluble peptoids to synthetic lipid membranes was quantified using second harmonic generation (SHG), a laser-based spectroscopy technique. In our experiments, SHG was used to measure biologically relevant peptoid concentrations at the aqueous-bilayer interface. Peptoid structure (length, substituent identity, charge) and membrane composition (lipid identity, cholesterol content) were varied. Additionally, zwitterionic lipid membranes were doped with cationic or anionic lipids to test electrostatic interactions. A molecular-level understanding of peptoid-lipid interactions will allow us to build models which we can use to predict the physiological implications of introducing peptoids into the human body.

COLL 247

Zigzag-shaped silver nanoplates: Synthesis, growth mechanism, and their application to highly sensitive strain sensors

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Zigzag-shaped Ag nanoplates display unique anisotropic planar structures with unusual jagged edges and relatively large lateral dimensions, and hence appear to constitute a promising candidate for metal inks in printed electronics, which can be used for realizing stretchable electrodes. Herein, we report the synthesis of zigzag-shaped Ag nanoplates via a one-pot coordination-based synthetic strategy where the reduction kinetics was manipulated. In the synthetic procedure, cyanuric acid acted as a ligand to form
complex structures with Ag$^+$ ions and as a capping agent to promote the lateral growth of the Ag nanoplates, and in this way played a crucial role in the formation of the zigzag-shaped structure. In contrast to previous studies that reported oriented attachment to be the predominant mechanism responsible for the growth of their zigzag-shaped nanoplates, Ostwald ripening explained the growth in the current work. Our findings on the particle morphology and crystalline structure of the Ag nanoplates motivated us to exploit them as conductive materials for stretchable strain sensors. Stain sensors based on nanocomposites of our zigzag-shaped Ag nanoplate and polydimethylsiloxane (PDMS) in the form of a sandwich structure were successfully produced by following a simple, low-cost and solution-processable method. The strain sensors exhibited extremely high sensitivity (gauge factor » 2,000), high stretchability (» 27%) with linear responses, and high reliability, all of which allowed the sensor to monitor diverse human motions, including joint movement and phonation.

**COLL 248**

**Metal nanocrystal-based sensing platform for the quantification of water in water-ethanol mixtures**

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Triangular silver (Ag) nanoplates with sharp corners exhibit fascinating optical properties, but their triangular shapes are not thermodynamically stable. However, this intrinsic instability can be used to realize novel applications. In the current work, we designed such application, one in which the spontaneous rounding of the sharp corners of the Ag nanoplates exposed to bromide ions (Br$^-$) was used to develop a novel sensing platform for the quantification of water in water-ethanol mixtures. The rate of change of the color and spectral features of a water-ethanol mixture containing Ag
nanoplates resulting from the introduction of KBr was found to be strongly correlated with the volume fraction of water in the mixture. This relationship, which was attributed to the previously determined dependence of the solubility of KBr on the volume fraction of water in water-ethanol mixtures, allowed for the quantification of water in water-ethanol mixtures having any water volume fraction (from 0 to 1.0). This colorimetric sensing platform exhibited reliable sensing results in real water-ethanol mixture samples and it was also successfully applied to determining the relative amount of water in water-isopropyl alcohol mixtures, suggesting that it could furthermore be applied to mixtures of water and other alcohols as well. We believe that the nanocrystal-based sensing platform holds great potential for use as a point-of-care analytical tool for the quantification of water in the fine chemical, pharmaceutical, and food and beverage industries.
Exciton dynamics in colloidal covalent organic frameworks

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Covalent organic frameworks (COFs) are an emergent class of polymeric materials defined by their crystallinity, permanent porosity, and modularity. By varying the identity of monomeric components, these materials' structure and function can rationally be designed for use as chemical sensors, photovoltaics, photocatalysts and more. However, implementation of these materials into devices has faced limited success due to their low quality, polycrystalline nature; these materials had not achieved their desired crystalline structure due to small domains aggregated in random orientations to each other. Expanding on an earlier study in which single crystalline two-dimensional COFs as solution stable colloids were synthesized, we perform high quality optical characterization via ultrafast spectroscopy. Exciton dynamics of COFs are examined via a power dependent transient absorption study of COF-5. By performing transient absorption in the high fluence regime, exciton-exciton annihilation kinetics were investigated to determine exciton diffusion lengths. Comparing exciton-exciton annihilation kinetics across a number of different sizes of COF-5 colloids revealed a crystallite size dependence to exciton-exciton annihilation dynamics, unveiling the effect of colloid domain size on excitonic transport in these materials.

COLL 250

Porphyrin macrocycles linked to surfaces by centrally coordinated Si-O bridges

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The influence of silicon tetrachloride as a coupling agent for the surface assembly of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) on Si(111) was investigated using atomic force microscopy (AFM). Nanopatterned films of porphyrins were prepared using particle lithography to evaluate the morphology, thickness and molecular orientation of Si-OEP films. Porphyrins have a macrocyclic tetrapyrrole structure which may be functionalized with various substituents. Modifications of the macrocycle, peripheral groups or bound metal ions can generate a range of electrical and photoelectrical properties. When preparing surface films, the planar macrocycles of porphyrins spontaneously self-associate to form stacked structures. This natural capability of self-stacking poses a challenge for developing processes for molecular patterning. When preparing films, porphyrins associate by electrostatic interactions between macrocycles as well as physisorption to the substrate to form coplanar arrangements of stacks of molecules, analogous to a stack of coins. The orientation of porphyrins on surfaces is also affected by the nature of the peripheral substituents and their position on the
macrocycles. We introduced silicon tetrachloride to the porphyrin reaction vessel to mediate coupling between the surface and porphyrins through covalent interactions. Protocols of particle lithography were used as a nanoscale patterning tool to prepare well-defined surface structures and films of OEP. Our goals are to correlate nanoscale properties (conductance, photocurrent generation) with designed surface structures of porphyrins in which the coupling between the surface and porphyrins is mediated by covalent interactions. Conceptually, by arranging and orienting the macrocycles of porphyrins with defined orientation, local surface measurements can be addressed questions about how structure influences properties.

Nanodots of Si-OEP deposited within a matrix film of Octaethyltrichlorosilane viewed with AFM topography images

**COLL 251**

**Tuning the sensing performance of multilayer plasmonic core-satellite assemblies for rapid detection of targets from lysed cells**

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Optical sensors based on discrete plasmonic nanostructures are very attractive for probing biomolecular interactions at the single-molecule level and have been applied as single nanoparticles or plasmonic rulers or reconfigurable multi-nanoparticle assemblies. However, their adaptation as a versatile sensing platform is limited by the research-grade instrumentation required for single-nanostructure imaging and/or spectroscopy and complex data fitting and analysis. Additionally, the dynamic range is often too narrow for the quantitative analysis of targets of interest in biodiagnostics, food safety or environmental monitoring. Herein we present plasmonic assembly comprising a core nanoparticle surrounded by multiple layers of satellite nanoparticles through
The layer-by-layer assembly of the satellite nanoparticles yields uniform discrete nanoparticle clusters on a substrate with enhanced optical properties. Binding of the model target (adenosine 5'-triphosphate, ATP) induces disassembly and leads to a dramatic decrease in the scattering intensity that can be analyzed readily from darkfield images. The sensing performance of assemblies, such as detection limit, dynamic range and sensitivity, can be tuned by controlling the size of the assembly. Furthermore, by assembling the clusters on a flexible support, cellular ATP can be directly detected by lysing adherent cells in close contact with the sensor – a process that does not require any sample preparation or purification. Enhancing the optical detection signal via designing and engineering nanoparticle assemblies could enable their use with low-cost portable imaging systems and broaden their applicability beyond the study of biomolecular interaction.

Direct detection of ATP from cell lysate

COLL 252

Influence of calcite on uranium(VI) sorption onto montmorillonite clay

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Currently, most proposed methods for the long-term storage of nuclear waste include engineered buffer systems (EBS) in underground geologic repositories. The design of EBS typically involves a layer of geological buffer material such as bentonite. Bentonite is an ideal material for these systems, since it largely consists of the swelling smectite clay montmorillonite, which provides two types of surface sites available for the sorption of radionuclides, such as uranium(VI) (U(VI)). However, the presence of calcite, a common accessory mineral in bentonite, may potentially alter the sorption of U(VI) onto montmorillonite in multiple ways. First, calcite provides an additional surface for U(VI) sorption reactions. In addition, calcite dissolution will lead to dissolved calcium in porewater solutions, which may in turn affect U(VI) solution speciation, U(VI) ion exchange reactions, and the stacking and interlayer spacing of smectite layers. Last, a potential formation of U(VI)-Ca-carbonate co-precipitates may remove U(VI) from solution.

As a first step, we characterized the sorption of U(VI) onto montmorillonite in the presence and absence of dissolved calcium at various ionic strength conditions in batch
sorption envelope experiments. The presence of dissolved calcium resulted in decreased U(VI) sorption onto montmorillonite in acidic environments, but in no apparent changes in U(VI) sorption in near-neutral pH ranges. At higher pH values, there may be a possible decrease in U(VI) sorption, which needs to be further investigated. The observed trends at low pH can be explained by the preferential binding of Ca$^{2+}$ cations relative to UO$_2^{2+}$, which resulted in a competition between the two cations for clay surface sites. This hypothesis is further supported by the results of additional sorption experiments, which were performed at various ionic strengths, but in the absence of calcium. In a next step, we will expand our experiments to include mixtures of calcite and montmorillonite as solids.

**COLL 253**

**Synthesis and design of biomimetic conductive nanocomposites to enhance key surface adsorption phenomena in microbial fuel cells**

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Microbial fuel cells (MFCs) have emerged as a potential renewable energy source due to their ability for direct conversion of organic substrates into electrical energy. However, the practical application of this technology is hindered by low power density, limited long-term stability, and high operational costs. More specifically, one main factor impacting fuel cell performance is the bacterial interactions at the electrode interface and the associated electron transfer mechanisms. In an effort to increase productive interactions between the microbes and anode, this work focused on the synthetic design of a cellulose-based, nanocomposite material. The biomimetic electrode surface was modified via non-covalent linkages of organic fuels, such as glucose and lactate, with TiO$_2$ nanoparticles to decrease bacteria-surface repulsions. Additionally, incorporation of β-cyclodextrin (β-CD), a supramolecular amphiphilic molecule, was used to constrain mediator adsorption to the surface of the cellulose matrix. The synergistic relationship between additives was investigated to modulate bacteria and mediator interactions at the electrode interface to ultimately increase the electron transfer efficiency. When compared to the industry standard carbon cloth materials, the composite electrodes had improved electrical response characterized via power density, polarization, and cyclic voltammetry for both *E. coli* and *S. oneidensis* MFC systems. Electrical output and bacteria-surface interactions were correlated using atomic force microscopy (AFM) and epifluorescent optical microscopy to determine biofilm formation and cell viability. Initial results show that the sugar functionalized electrodes demonstrated an increased electric response in conjunction with photochemical activity. This phenomenon was observed through decreased fluorescence intensity without a decrease in cell viability as well as increased open circuit potential in the presence of light. This ligand-metal charge transfer coupled with increased conductivity of a biomimetic bulk material has resulted in an overall improved MFC system.
Coll 254

Comparing the optical properties of \( \text{Au}_{25} \) icosahedral and bi-icosahedral clusters

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Structure and reactivity of super atom gold clusters depends on the electronic interaction between core gold atoms and the ligand. The super atom clusters of the dimension 1.1 nm containing 25 atoms of gold and 18 ligands, can be of two shapes - spherical (icosahedral; comprised of core and shell gold; made of thiol (SR) ligands; \( \text{Au}_{25}\-i \)) and rod shaped (bi-icosahedral; comprised of core and bridging gold atoms; made of SR and triphenlyphosphine (PPh\(_3\)) ligands; \( \text{Au}_{25}\-bi \)). Both clusters are photoluminescent (PL) but \( \text{Au}_{25}\-bi \) has higher quantum yield. In this project we push the loading of chromophores on the nanoparticle surface and compare the changes in PL as a function of geometry. Ground state electron transfer is monitored via voltammetry to investigate the direction of electron flow. The influence of the chromophore (modified and anthracene) will be ascertained by two-photon cross-sectional measurements and steady state measurements.

Coll 255

Self-assembled monolayer functionalization of gold nanostar particles with a custom designed carboxylate-terminated dithiol as a linker for bioconjugation

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This presentation reports the reproducible synthesis of gold nanostars (GNSs) based on a seed-growth method and their functionalization with a custom-designed carboxylate-terminated dithiol. Multiple extinction bands in both the visible as well as the near-infrared (NIR) range are exhibited by these pointy nanoparticles. Importantly, their NIR extinction maximum at ~970 nm allows for excitation using wavelengths of light that can penetrate through human tissue. Furthermore, functionalization of the surfaces of the stars using carboxylic acid-terminated thiol molecules as self-assembled monolayers (SAMs) enables bioconjugation (e.g., with antibodies) and utilization in various biological applications, such as nanosensors, biological assays, and drug delivery. The GNSs were analyzed by scanning electron microscopy (SEM) to validate their star-like shapes, as well as X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy to verify their chemical composition. The use of these nanostars in biological assays will be described. In particular, the effect of the star
morphology on the ability of the nanoparticles to bind to various functionalized surfaces will be discussed.

**COLL 256**

**Methane hydrate formation and dissociation: On the effects of different porous materials**

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Effects of porous materials on methane hydrate formation and dissociation were investigated in a quiescent system. Activated carbons (AC) and hollow silica (HS) were chosen to reflect different hydrophobicity and density of the materials. The methane hydrate formation experiments were carried out at 6 and 8 MPa and 4°C. Tetrahydrofuran (THF) was also used to facilitate the hydrate formation. Without any porous materials nor THF, there was no methane hydrate formed after 48 hours. At both pressures and 4°C, the presence of AC induced the hydrate formation. However, the methane uptake was lower with 6 MPa. In addition, there was multiple hydrate formation regardless the pressure. With HS, the methane hydrate formation formed at a much higher rate than with AC. In addition, the methane uptake was higher with the presence of HS. That is likely due to the structure and the degree of hydrophobicity of HS that promote the interaction between the methane gas and water to form methane hydrate at a much faster rate. The combination of THF with either AC or HS significantly increased the methane hydrate formation and methane uptake. For methane dissociation, the presence of HS facilitated the methane dissociation at a greater extent. With the porous materials, it is now possible to increase the hydrate formation at a much greater rate.

**COLL 257**

**Synthesis of germanium nanoparticles by rapid inductive heating**

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Magnetic inductive heating provides an alternative methodology to hot injection approach in nanoparticle synthesis. In this work, this methodology is applied to synthesis of Germanium nanoparticle. Germanium nanoparticles are useful as an anode in lithium ion batteries with high capacity and excellent cycling stability. Inductive heating provides rapid temperature raise that is required for nucleation and growth of nanoparticles for colloidal synthesis. We demonstrate synthesis of Germanium nanoparticles using the mixture of GeI₂ and GeI₄ as a precursor and oleylamine as a solvent with in few seconds (5sec,10sec). The size- controlled synthesis can be achieved with the change in the concentration of precursor. Here, oleylamine acts as a solvent, reducing agent and binding ligand as well. This method is considered safer because it avoids the use of strong reducing agents (NaBH₄, LiAlH₄) and etching agents
like (HF). The synthesized nanoparticles are characterized by TEM, XRD, UV-Visible spectroscopy, Raman Spectroscopy and FTIR spectroscopy.

COLL 258

Effect of *Ficus tikoua* leaves extract as an eco-friendly inhibitor of carbon steel in HCl solution

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A renewable and biodegradable carbon steel corrosion inhibitor in HCl solution based on Ficus tikoua leaves extract were investigated with the methods of electrochemical experiments, morphological characterization measurements and theoretical calculations. The polarization curve measurements illustrated that this Ficus tikoua leaves extract performed as mixed-type inhibitors with a good inhibitive ability. The efficiency of the inhibitor increased with the increase of concentration, reaching 95.8% at 298 k when the dosage was 200 mg/L. In addition, corrosion experiments at different test temperatures showed that the extract has a good inhibition ability in a wide range of temperatures. The results were further confirmed by morphological analysis. Furthermore, the theoretical calculation shows that some components of the corrosion inhibitor have good corrosion inhibition performance. There is good agreement between electrochemical experiments and theoretical calculations. This work provides some valuable guidance for the use of plant extract inhibitors to inhibit corrosion of carbon steel in hydrochloric acid.

COLL 259

Analyzing the surface Interactions of a myelin sheath Langmuir model membrane system with the addition of quercetin

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The myelin sheath membrane is an integral component of the central nervous system that is wrapped tightly around the axons segments of nerve cells. It functions as an insulator that speeds up the impulses through the nerve fibers. The membrane is comprised of phospholipids, cholesterol and proteins. In this study, the Langmuir Monolayer technique is utilized to investigate the interactions that transpire between lipids and proteins that are found in the myelin sheath membrane upon the addition of a flavanol, Quercetin, found in *Ginkgo biloba*. The lipids used were a Brain Lipid Extract, Sphingomyelin, DPPC, and Sulfatide. The Langmuir Monolayer technique was used as an experimental model of the lipid membrane, and through the observation of the changes in surface pressure and molecular area, the degree of order or fluidity was inferred. Experiments were carried out using a Kibron trough; the membrane
components were deposited onto Phosphate Buffered Saline sub-phase with a pH of 7.4. A comparison of the results give indication of the fluidity of the model membrane with the addition of Quercetin.

**COLL 260**

**Heterogeneous catalytic upgrading of long-chain alkenones derived from microalgae**

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Biomass derived from *Isocrysis* microalgae is a promising feedstock for biofuel production. Among the compounds extracted from the microalgae are polyunsaturated long-chain (C36-C40) alkenones that represent an interesting substrate for upgrading to fuel fractions. Past research has focused on homogenous catalyzed conversion, but a heterogeneously catalyzed process has greater potential for up-scaling and economic viability. Acidic sites are needed for C-C cleavage and isomerization while metallic sites are important for hydrodeoxygenation (HDO) and hydrogenation of cleaved species. The tuning of these catalytic sites can play a pivotal role in determining the activity and selectivity of bifunctional catalysts. With this in mind, we are investigating the properties of Ni, Ni2P and noble metals (e.g. Pt-Re) on amorphous silica-alumina (ASA) and zeolite (USY) supports for alkenone conversion. The catalysts were prepared by incipient wetness and characterized using X-ray diffraction, electron microscopy and nitrogen adsorption (surface area, pore size). Alkenone conversion is under investigation using a fixed-bed reactor with the reactor effluent analyzed via gas chromatography. Initial catalytic studies indicate high alkenone conversion below 200 °C, with a product distribution that depends strongly on the metal/support combination.

**COLL 261**

**Transition metal mediated bioorthogonal catalysis with controlled localization and kinetics for nanotheranostics**

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Transition metal catalysts (TMCs) can catalyze a wide variety of chemical transformations, making them potential tools for bioorthogonal catalysis. We recently demonstrated that TMCs can be encapsulated in the surface monolayer of nanoparticles (NP), generating water-soluble “nanozymes”. These nanozymes demonstrate catalysis reminiscent of enzymes but can also catalyze a variety of
bioorthogonal processes. We report a rational approach to control the localization and kinetics of nanozymes by fine-tuning their surface chemistry. We demonstrated intra- extracellular catalysis by surface engineering of the nanozymes. We used membrane- penetrating cationic nanoparticles for catalysis inside and ‘stealth’ zwitterionic particles to limit catalysis to outside of mammalian cells. Specific localization of nanozyme activity was demonstrated through profluorophore activation. Therapeutic efficacy was demonstrated through intra- and extracellular activation of a prodrug. Further, we fabricated nanozymes possessing different surface hydrophobicity to regulate their interaction with a library of profluorophore substrates. We determined that nanozyme catalysis efficiency was driven by supramolecular interactions between the nanozymes and substrates. This study of nanozyme surface engineering provides the nanozymes with specific localization and tunable catalysis reminiscent of their enzyme prototypes.

COLL 262

Continuous and scalable synthesis of Pt multipods with enhanced electrocatalytic activity toward oxygen reduction reaction

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Platinum nanocrystals with various shapes have been extensively studied to improve their catalytic performances toward the sluggish oxygen reduction reaction (ORR) in a proton-exchange membrane fuel cell. In particular, Pt multipods have attracted much attention due to their open branched structures and intrinsically high surface area. A number of strategies have been developed for the synthesis of Pt multipods, but the synthetic procedures could be complicated and it’s still challenging to scale up the production. We developed a facile technique for the scalable production of Pt multipods with small sizes and branched structure in a continuous flow system. The synthetic protocol was simplified by using oleylamine as the solvent, surfactant and reducing agent. It was proposed that the combination of fast autocatalytic surface growth and small particles attachment contributed to the anisotropic growth of Pt multipods. Compared with the batch-based synthesis, the throughput of the production in the flow system can be increased to 17 mg of Pt per hour with tight control over the quality of the products. Owing to the open branched structure, Pt multipods/C catalyst exhibited enhanced activity toward oxygen reduction reaction when benchmarked against the commercial Pt/C catalyst.

COLL 263

Study of structure-property relationships of methoxylated sucrose soyate polyol self-assembly
Lipid-based, nanoscale molecular transporters have found applications in the areas of pharmaceutical sciences, diagnostics, nutritional sciences, and in cosmetic industries. These soft colloids have been developed to improve stability and functional properties of the encapsulated content. This is particularly important for designing efficient drug and nutraceutical delivery systems (DS), as lipid nanocarriers present the promise of enhancing bioavailability, biodistribution, solubility and transport capacity of many hydrophobic molecules or poorly water-soluble molecules.

We prepared fully bio-based nanocarriers termed ‘Soysome’ composed of Soybean derived fatty acid polyols conjugated to sucrose (methoxylated sucrose soyate polyol, MSSP). The advantages of such biobased materials are: (a) low cost access to the final product, (b) facile post-synthetic modification (c) biocompatibility by design, and (d) abundant commercial affordability. Using a facile nanoprecipitation technique, we demonstrated that upon solvent shifting (Ouzo technique), MSSP forms stable, surfactant-free, self-assembled structure of size range within 50-150nm and narrow polydispersity index (Figure1). Particle size of Soysomes can be varied systematically by careful selection of solvent-pairs during their preparation. We are currently studying Soysomes to evaluate their encapsulation and release capacities towards hydrophobic guest molecules ranging from chemotherapeutic agent, such as paclitaxel to a nutraceutical, such as curcumin. We investigated different physico-chemical factors governing colloidal behavior of Soysomes particles. Understanding the mechanistic properties of Soysome could open exciting avenues for use of renewable resources to generate smart colloidal materials amenable towards multifarious industrial applications.
Soysomes formed from MSSP nanoprecipitation/ solvent shifting and the identification of the stable "Ouzo" region

**COLL 264**

**Design of a supramolecular photocatalytic nanocomposite for the remediation of heterogenous wastewater**

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As the use of textile dyes, pesticides, and heavy metal ions (HMI) in the industrial and agricultural sectors have increased, sequential iterations are often required in wastewater treatments. Current research has shifted towards alternative methods that allow for the remediation of wastewater using cost-effective materials. More specifically, naturally abundant polymers, such as cellulose and its common derivatives, have gained attention due to their high adsorptive properties and tunable morphology. A supramolecular-photocatalytic nanocomposite was designed to efficiently remediate a broad range of model pollutants (methylene blue (MB), cadmium ions (Cd²⁺), Roundup®, and parabens), through the incorporation of titanium dioxide (TiO₂) and β-cyclodextrin (β-CD) into a bulk cellulose material. Initial results show that the synthesized nanocomposite demonstrated effective pollutant remediation through non-covalent interactions. The relationship between TiO₂ and β-CD was modulated to alter the performance of the cellulose-based matrix when utilized in heterogenous wastewater systems.

**COLL 265**

**Seed-mediated synthesis of bimetallic copper-nickel nanoparticles for catalysis**

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The wide range of applications for metal nanoparticles makes them a major target for synthesis and testing for a variety of uses. Copper and nickel have been found to possess interesting properties relevant to catalysis applications, such as carbon dioxide reduction and hydrogenation reactions.¹ Here, we synthesized copper-nickel alloy nanoparticles with a variety of morphologies and elemental distributions by the controlled reduction of metal salts, primarily using a nickel nanoparticle seed-mediated methodology. The characteristics of the resulting nanoparticles, including morphology and elemental composition and distribution, are tunable based on reaction conditions such as ratios of starting materials, reaction temperature, and the identity of the reducing agent. Copper and nickel are completely miscible in bulk; interestingly, our
method produced dumbbell-shaped nanoparticles in which the two metals were separated to some degree, with each end of the dumbbell composed of a different metal. In these cases, alloy formation was very limited, and in some cases the separation was almost complete. Characterization was accomplished by UV/Vis spectroscopy and TEM and SEM imaging, and elemental mapping via STEM-EDX. The products were reasonably monodisperse, with consistent compositions and shapes. The nanoparticles were synthesized for the determination of their efficacy in catalyzing the reduction of carbon dioxide to higher-order products.

COLL 266

Core-size conversion of plasmonic gold nanomolecules

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The gold nanomolecules have a distinct number of gold atoms and thiolate ligands, with a molecular formula of the form $\text{Au}_x(\text{SR})_y$. The nanoparticles of size less than 3 nm are nanomolecules which are atomically monodisperse, whereas nanoparticles in 3-100 nm range are monodisperse in size but not atomically monodisperse i.e. they do not have a distinct number of atoms. Each ligand has a unique series of gold nanomolecules with a distinct number of gold atoms and ligands. The optical properties of the molecule-like nanomolecules vary significantly from the bulk gold possessing discreet electronic structures. As the size increases the surface plasmon resonance (SPR) is observed at a threshold point indicating the onset of metallic properties. The heterogeneous ligands are known to induce changes within a nanostructure and composition, which also induces changes in the unique properties of the material. The different core size conversions that have been reported to date are conversions of molecule-like nanomolecules. For example: $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$ to $\text{Au}_{133}(\text{SPh-fBu})_{52}$, $\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}$ to $\text{Au}_{99}(\text{SPh})_{42}$, $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ to $\text{Au}_{36}(\text{SPh-fBu})_{24}$, $\text{Au}_{38}(\text{SCH}_2\text{CH}_2\text{Ph})_{24}$ to $\text{Au}_{30}(\text{S-fBu})_{18}$, etc. Here, we report the first plasmonic core size conversion of plasmonic $\text{Au}_{329}(\text{SCH}_2\text{CH}_2\text{Ph})_{84}$ to plasmonic $\text{Au}_{279}(\text{SPh-fBu})_{84}$ nanomolecules. The reaction has been studied using electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) mass spectrometry and absorption spectroscopy.

COLL 267

Growth and characterization of bimetallic metallic-organic framework films

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Metal-organic frameworks (MOFs) are porous, crystalline materials constructed from organic linkers and metal nodes in which the structure, geometry, and distribution of metal sites can be well controlled and characterized. These new materials have applications in gas purification, storage and separation processes, as well as heterogeneous catalysis. In addition, recent studies have shown that the electronic properties of MOFs can be tuned by substitution of a second metal into the metal nodes. Crystalline films of Cu₃(BTC)₂ (BTC³⁻=benzene-1,3,5-tricarboxylate) have been grown on a single-crystal Si or alumina/Si support via sequential dip-coating in solutions of Cu(CH₃COO)₂ and H₃BTC/ethanol. Bimetallic films are prepared by immersing the CuBTC film in a solution of the second metal ion (Co²⁺, Rh³⁺), and X-ray photoelectron spectroscopy (XPS) confirms the incorporation of the second metal. The crystallinity of the films is established by grazing incidence wide-angle X-ray scattering, and film morphologies are characterized by atomic force microscopy. Furthermore, the nature of adsorption sites in the MOF films is explored by temperature programmed desorption of probe molecules like CO. Valence band XPS provides information on electronic properties by probing the density of states near the Fermi level.

**COLL 268**

Tuning the surface ordering of self-assembled ionic surfactants on semiconducting single-walled carbon nanotubes: Concentration, tube diameter, and concentrations

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Understanding the self-assembly of surfactants on the surface of single-walled carbon nanotubes (SWCNT) is important to decipher and improve separation techniques of metallic and semiconducting SWCNT and their application in nano electronics and sensing. In this study, we report direct spectroscopic measurements of the macromolecular organization of surfactant ordering using different concentrations of sodium dodecyl sulfate (SDS) encapsulated with defendant diameter (6,5) and (7,6) semiconducting SWCNTs with and without excess electrolytes within solution-processed thin films. By using vibration Sum Frequency Generation Spectroscopy (VSFG), sensitive measurements of interfacial surfactant ordering, we find that as the bulk SDS concentration increases near the surfactant critical micelle concentration (CMC) the interfacial order increases as well, independently of SWCNTs diameter. However, at higher surfactant concentration measured here, the (6,5) SWCNTs produce more ordered structures relative to those with (7,6) SWCNTs. The relatively larger diameter (7,6) chiral tubes support enhanced van der Waals (vdW) interactions between the tube surface and the surfactant alkyl chain groups that increase the density of gauche defects. A new effect arises when the precursor solution
is exposed to a small concentration of divalent Ca\(^{2+}\)-counterions. We postulate that the salt bridging configuration on such highly curved surfaces decreases the ordering of interfacial surfactant molecules. However, this phenomenon was not observed with excess Na\(^+\) ions at the same ionic strength, where instead a modest increase in surfactant ordering was observed with the excess monovalent electrolyte. These results provide significant insights for solution processing of vdW nanomaterials and demonstrate that VSFG is a sensitive probe of nanostructured.

**COLL 269**

**Stabilizing enzyme on carbon nanotubes with metal-organic frameworks for enzyme delivery and biocatalysis applications**

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Carbon nanotubes (CNTs) are advanced nanoscale platforms for enzyme immobilization and targeted enzyme delivery. Covalently linking enzyme to CNT surfaces is challenged by the potential enzyme modification as well as the controlled release for delivery applications. Physical adsorption of the enzyme to CNT based on electrostatic and other non-bonding interactions avoids these barriers but suffers from leaching. A potential solution is to use Metal-organic framework (MOF) to stabilize enzymes on CNTs which does not require any enzyme chemical modification. MOFs also provide extra stability under harsh environments. A special MOF, Zeolitic Imidazolate Framework (ZIF), is pH-sensitive, making the controlled release of the immobilized enzyme possible. The challenge in using MOF/ZIF to stabilize enzymes on CNTs is to understand and fine-tune the properties of enzymes, such as orientation, conformation, and distribution in the CNT/MOF composites. This is a non-trivial task for most biophysical technique because of the complexities caused by the background signals of CNT and ZIF, as well as the interactions between the enzyme and the platform. In this work, we report, for the first time, the preparation of enzyme/CNT/ZIF nanocomposites. In addition, we utilize a unique technique, Site-Directed Spin Labeling (SDSL) in combination with Electron Paramagnetic Resonance (EPR) spectroscopy, which is immune to aforementioned technical barriers, to probe the structural insights of the enzyme in the composites. For proof-of-concept, we employed two model enzymes, lysozyme, and amylase, for our studies. In comparison to CNT only, we found enhanced restriction and stability of lysozyme on CNT in the presence of ZIF as confirmed by a set of biophysical tools. Activity assays also confirmed that both enzymes are active on CNT/ZIF composites. The results are informative for guiding the rational design of CNT/ZIF combinations to improve stabilization, loading capacity, and catalytic efficiency.

**COLL 270**

**Immobilized antioxidants and their radical scavenging activity**
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Bare, anionic-type antioxidants (curcumin, glutathione, ellagic acid, ascorbic acid, chlorogenic acid, etc.) and their composites with layered double hydroxides (LDHs) were under investigation. The composites were prepared via co-precipitation and the effect of post-synthetic hydrothermal treatment (HT) and aqueous miscible organic solvent treatment (AMOST) was evaluated. The hybrid materials have remarkable antioxidant-content while maintaining the structure of the carrier and no by-products were formed. We found that AMOST improves the dispersability of the samples in water and methanol, therefore favoring the scavenging activity in colloid state. For antioxidant activity measurements, superoxide dismutase (SOD), 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging activity and cupric reducing antioxidant capacity (CUPRAC) tests were involved. We hope that the samples can act as reactive oxygen species (ROS) scavengers \textit{in vivo} experiments.

COLL 271

Dynamic self-assembly of quasi-1D and 3D structures in rotating fluids

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Dynamic self-assembling systems, those that function in out-of-equilibrium and require continuous energy supply to sustain the formed structure, are ubiquitous in nature and have also shown that it can be artificially created in unnatural system. Nature of residing away from equilibrium allows dynamic system to produce complex spatiotemporal patterns or structures that are not usually obtainable from static self-assembling system. Despite this high potential for creating diverse structures, a dynamic system exhibiting highly ordered structure or rich phase behavior has not been extensively exploited except for a few exceptions. In this study, we describe dynamic self-assembly of quasi-1D and 3D structures which relies on inertial force imposed by a rotating fluid denser than the assembling particles as well as drag force applied by conical vortices arising from the rotors positioned in the fluid. The dynamical system consists of polymeric spherical particles placed in a cylindrical tube which is filled with a denser fluid. The particle’s size ranges from a few hundreds of micrometers to a few millimeters. When the tube rotates at speeds higher than a threshold (~500 RPM), the centripetal force can confine the particles on the tube’s axis. Depending on the sizes and numbers of the particles, the system can form mono-component and binary quasi-1D structures ranging from those having many ($D_{4d}$, $D_{6h}$, etc.) to very few ($C_1$, $C_3$) symmetry elements. On the other hand, it is also possible to generate 3D structure by imposing additional
constraints on the system. We adopted contactless magnetic damping of a conductive material (i.e. eddy current brake) to create a whirling vortex which applies drag force on the particles in an axial direction. With systems under the effect of the centripetal force coupled with the conical vortices, we demonstrated the formation of simple molecular structures, anisotropic packings induced by jamming of particles, and polymorphic structures composed of 13 spherical particles. We surmise that this modality of rotational self-assembly can prove useful in preparing fibrous complex structures supporting radial gradients of composition and studying finite packings of diverse assembling components.

COLL 272

Probing the interactions between polymeric filtration media and nanoparticle dispersions relevant to copper (Cu) Chemical Mechanical Planarization (CMP)

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Chemical Mechanical Planarization has emerged as a critical technology for the planarization of precision optical components, data storage media, and integrated circuit (IC) semiconductor devices. This process balances chemical surface modification and mechanical removal utilizing a nanoparticle dispersion (slurry) to limit defects and irregularities with the goal to attain angstrom level uniformity. The chemical components of a model Cu CMP slurry include abrasive particles, corrosion inhibitors, complexing agents, oxidizing agents, and pH adjusters. The traditional abrasive used in the Cu CMP slurry is silica (SiO$_2$) due to its stability and selectively for the Cu surface. As technology continues to advance, CMP slurries are increasing in complexity, making it necessary to implement a filtration process that works to capture rogue particles that are known to have a significant effect on defectivity. In order to unravel the dynamic synergy between the slurry formulation and filtration media, it is essential to investigate the role of media surface energy on filtration performance. More specifically, this work set out to probe the noncovalent interactions that control slurry/polymer adsorption using a model Cu CMP slurry on polyamide and polypropylene based media. Current results have shown that the filtration process has a significant impact on the slurry integrity, which can be correlated to changes in the complexing/passivation agent synergy. Monitoring these changes was performed via Cu removal rate, dynamic light scattering (DLS), zeta potential, electrochemical quartz crystal nanobalance (EQCN), and potentiodynamic scan analysis as a function of the filtration process. Ultimately, results indicate that the filtration process is effective in removing rogue particles, but has shown to have an impact on chemistry adsorption to the media which directly impacts the activity of the slurry during the CMP process.

COLL 273
Self-assembly of functionalized carbon nanoparticles on polyurethane foam for low-cost water purification

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Pollution now affects almost all bodies of water on earth and in developing countries, the ability to provide clean water has been hindered by a lack of infrastructure and high costs. The development of new materials and techniques to improve water purification is an area of active research and the search to lower the economic barriers to provide clean water is an on-going challenge. In this study, we report the development of a multi-functional and inexpensive adsorbent that is prepared through the evaporation mediated self-assembly of acidic carbon nanoparticles on common polyurethane foam. The carbon nanoparticles were prepared through the simple, one step, acid dehydration of glycerol, and were found to contain many functional groups including sulfonic acid (2.5 mmol/g), carboxylic acid (2.5 mmol/g), and hydroxyl (5.1 mmol/g) functional groups. The carbon materials were suspended in ethanol and deposited on common polyurethane foam using simple evaporative self-assembly. The coated foam was found to be extremely effective at removing common contaminants including lead, cadmium, and methylene blue and both the thermodynamics and kinetics of adsorption were evaluated. The practical application of the foam for pollutant removal was tested using a rapid small-scale column technique (RSSCT) and the breakthrough curves were evaluated and fit to the Thomas model. The columns could be easily regenerated with 0.1M nitric acid and recycled many times without losing adsorption capacity. The carbon nanoparticle coated polyurethane foam showed the enhanced ability to remove common contaminants and can be easily incorporated into large-scale filtration systems.

COLL 274

Synthesis and antibacterial enhancement of biomimetic hydrogel matrices for wound management applications

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Traditional wound management materials have been shown to impede healing processes due to a lack of intimacy at the wound-material interface. Specifically, these materials exhibit poor adhesive, absorptive and antimicrobial properties which inhibit healing and increase risk of infection. To increase the efficiency of the healing process, focus has shifted to the development of wet wound management materials. These materials increase levels of moisture in the wound environment, which increase oxygen permeation to the wound and rates of cellular regeneration, but moisture also increases the probability of contracting clinically-acquired infections. Effective antimicrobial
functionalization of these materials has been achieved via incorporation of agents such as metal nanoparticles (MNPs) and antibiotics, both of which have preserved the biomimicry required for enhanced healing. This research demonstrates the synthesis of alginate-calcium polymer matrices functionalized with Ag and Au NPs. Ag NPs were synthesized using a photocatalytic reduction process, producing colloidal stable NPs at sizes up to 200 nm. For Au NPs, a chemical reduction pathway was used to produce 10-20 nm particles. Furthermore, Au NPs were functionalized with various antibiotics to promote increased levels of antibacterial activity. All NPs were characterized for initial antibacterial activity using a modified broth dilution method to measure the MIC of the agents. Finally, characterized particles were incorporated into alginate-calcium matrices and the antibacterial activity of these nanocomposites were probed using epi-fluorescent optical tweezers. Specifically, single E. coli cells were docked to the MNP-functionalized polymer matrix and cell death kinetics were measured in real-time via fluorescent indicators. Antibacterial activity of matrices modified with Ag NP was heavily dependent upon Ag concentration and size. Polymer matrices with Au NP incorporation showed minimal inhibitory effects with no antibiotic functionalization, but antibacterial activity increased substantially upon capping of Au NP with antibiotics.

COLL 275

**Investigating adsorption of methylene blue on single-walled carbon nanotubes using vibrational sum-frequency generation**

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Carbon nanotubes (CNTs) are a promising class of nanomaterials that possess the capability to purify wastewater from synthetic dyes such as methylene blue (MB). The efficiency to retain redox active MB dye provides insights to the development of novel cylindrical carbon-based nanomaterial for water purification from dye contaminants. Noncovalent interactions of methylene blue cation (MB⁺) adsorbed onto the curvature surface of semiconducting single-walled carbon nanotubes (SWCNTs) is characterized by using vibrational sum-frequency generation (VSFG) spectroscopy. This SFG technique looks at the vibrations specific to the surface and provides vibrational spectra of molecules solely at the interface. The adsorption of MB dye on the unique curvature surface of SWCNTs in solution has not yet been characterized, which limits the further advancement of the fabricated nanocomposites. Information from spectral measurements may provide insight to characterize the interfacial organization of MB⁺ ion adsorbed on SWCNTs in solution, and will attract further electrochemical studies and waste purification of cationic dyes.

COLL 276

**Detection of mercury ion using surface functionalized gold nanorods**
The gold nanorods (AuNRs) with their unique optical properties have shown lots of applications in the field of imaging, sensing and therapy. The longitudinal localized surface plasmon resonance (LSPR) is super sensitive to the surrounding local environment which makes AuNRs great candidates for the investigation of mercury detection. However, cetyltrimethylammonium bromide (CTAB) which is the most common capping ligand for AuNRs synthesis is the obstacle for high sensitivity of mercury sensing system. In our work, AuNRs were surface modified with polyelectrolytes via layer by layer method and used as sensor to detect mercury ions in the solution. The deposition of mercury on NRs was monitored by measuring the shift of LSPR. It was observed that due to the amalgam formation, the LSPR peak has a blue shift with the decrease of peak intensity. Furthermore, the relationship between CTAB concentration and AuNRs sensitivity confirmed that CTAB hindered the AuNRs sensing performance.

**COLL 277**

Use of dynamic light scattering for accurate sizing of gold nanoparticles with particular application to chemical and biological sensing

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Gold nanoparticles (AuNPs) have found extensive applications in chemical and biological sensing, catalysis, biomolecular imaging, in vitro diagnostics, cancer therapy, and many other areas. Dynamic light scattering (DLS) is a routinely used analytical tool for characterizing the size and size distribution of particles. DLS is the primary choice of instrumentation for analyzing nanoparticle suspensions because of its relatively low cost and ease of operation in comparison to other more sophisticated techniques. However, many DLS users are unfamiliar with the principles behind the DLS measurement and are unaware of some of the intrinsic limitations as well as the unique capabilities of this technique. This lack of sufficient understanding of DLS often leads to inappropriate experimental design and misinterpretation of the data. In this study, we performed DLS analyses on a series of AuNPs with diameters ranging from 10 to 100 nm. Our study shows that the measured hydrodynamic diameters of the AuNPs can vary significantly with concentration and incident laser power. The scattered light intensity of the AuNPs has a nearly sixth order power law increase with diameter, and the enormous scattered light intensity of AuNPs with diameters around or exceeding 80 nm causes a substantial multiple scattering effect in conventional DLS instruments. The effect leads to significant errors in the reported average hydrodynamic diameter of the AuNPs when the measurements are analyzed in the conventional way, without accounting for the multiple scattering. We present here some useful methods to obtain the accurate hydrodynamic size of the AuNPs using DLS. We also demonstrate and explain an extremely powerful
aspect of DLS and its exceptional sensitivity in detecting gold nanoparticle aggregate formation, and the use of this unique capability for chemical and biological sensing applications.

**COLL 278**

**Synthesis of all-inorganic Cd-doped CsPbCl$_3$ perovskite nanocrystals with dual-wavelength emission**

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Doped lead halide perovskite nanocrystals (NCs) have recently garnered significant attention due to their superior optoelectronic properties. Here, we report a new synthesis of Cd-doped CsPbCl$_3$ perovskite NCs achieved by decoupling Pb- and Cl-precursor sources in a hot injection method. The resulting Cd-doped perovskite NCs manifest a dual-wavelength emission profile with the first reported example of Cd-dopant emission. By controlling the Cd-dopant concentration, the emission profile can be tuned with a dopant emission quantum yield of up to 8%. The new secondary emission band (~610 nm) is induced by an energy transfer process from photo-excited host CsPbCl$_3$ NCs to Cd-dopants, and a subsequent electronic transition from the excited state ($^3E_g$) to the ground state ($^1A_{1g}$) of [CdCl$_6$]$^{4-}$ units. This emission mechanism is supported by a first-principles density functional theory calculation. Further, we demonstrate that the optical behavior of Cd-doped CsPbCl$_3$ NCs can be altered through post-synthetic Cl-to-Br anion-exchange reactions. Our studies shown here present a new model system for future doping chemistry studies in semiconductor materials which may influence various optoelectronic applications.
Broad bandwidth excitation profile acquisition for interfacial rhodamine dyes by doubly resonant vibrational-electronic difference-frequency generation spectroscopy

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The interface between bulk materials harbors unique chemical and physical properties. The ability to study the properties of interfaces in situ is essential in biologically, chemically, physically, and environmentally relevant systems. Sum and Difference-frequency generation (S/DFG) are non-linear spectroscopic techniques that have the capability to selectively probe the surface species and nearby solvation shell. Additionally, the signal is exquisitely sensitive to interfacial conformation, orientation and order. Herein we present a method of S/DFG spectroscopy using narrow IR pulses, resonant with a selected eigenfrequency of a vibrational mode, and broadband visible pulses used to probe the excitation profile of rhodamine dyes at a solid surface. Through the use of resonant IR pulses the DFG signal reports a doubly resonant excitation profile for the interfacial molecule in situ. This technique can be used to qualitatively study the effect of environment (i.e. pH, ionic strength) on the electronic properties as well as orientation of the analyte.

Self-assembly, thermal properties and gelation studies of acridine based cholesteryl carbamate as low molecular mass gelators

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Acridine based compounds have known to exhibit many biological functions. [1] In the present study acridine based cholesteryl carbamate has been prepared by the reaction between 9-aminoacridine and cholesteryl chloroformate as a potential low molecular mass gelator (LMG). A gelator molecule aggregate via weak interactions (e.g. H-bonding, π-π stacking) to form three dimensional self-assembled fibrillar networks and trap large amount of liquid. [2] The gelator design in this work is based on one of the common LMG structure (i.e., an aromatic moiety, a linker and a steroidal group).[3] 5 and 10 wt % of acridine based cholesteryl carbamate has been shown to gelate DMSO. Correlations between self-assembly and gelation properties of acridine based cholesteryl carbamate in various liquids and differential scanning calorimetric studies and spectroscopic properties of the synthesized carbamate derivatives will be presented.
Fluorescence detection of Fe$^{3+}$ using Salecan-derived nitrogen and phosphorus doped carbon dots and cell imaging

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Herein, we have reported a simple, but more effective strategy for the fabrication of blue-emitting N,P-CDs using Salecan and diethylenetriaminepenta (methylene phosphonic acid) as the precursors through a simple hydrothermal process. The quantum yield of N,P-CDs is as high as 48% by using quinine sulfate. HRTEM image of N,P-CDs shows well-dispersed in water solution. The particle size histogram shows the sizes to be around 2.8–4.8 nm with an average size of 3.6 nm and possess an almost globosity. The prepared N,P-CDs has remarked water-solubility, high biocompatibility, as well as excellent stability even under broad pH range (2–10), ionic strengths, and light illumination. The N,P-CDs could responses to Fe$^{3+}$ selectively and sensitively, while other metal ions show either no or slight change in the fluorescence intensity relative to the free N,P-CDs. There exists a fine linear correlation ($R^2 = 0.9969$) between the intensity and the concentration of Fe$^{3+}$ in the range of 0 to 60 μM with a detection limit of $8.18 \times 10^{-8}$ mol/L, which makes this material a suitable candidate for environmental Fe$^{3+}$ detection. Eventually, besides of its excellent biocompatibility and lower cytotoxicity, this carbon material also can be efficiently taken up by A549 and HEK 293T cells and can be used for intracellular Fe$^{3+}$ sensing and cell imaging, which indicated its potential applications.
Stability of spin cast poly(vinyl alcohol) thin films on polydimethylsiloxane

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Surface modification to achieve desirable surface properties is an important practice in materials science. A necessary criterion in evaluating the efficacy of a modification method is the stability of the modified materials under working conditions. Polydimethylsiloxane (PDMS) is a widely used polymer with unique chemical and physical properties. Many of its applications in aqueous media are limited due to its hydrophobicity. Poly(vinyl alcohol) (PVOH) has been shown to spontaneously adsorb to hydrophobic substrates from aqueous solution to impart hydrophilicity. The process is driven by hydrophobic interactions as well as crystallization of PVOH chains. Recently, we developed the adsorptive spin casting method by combining the spontaneity of adsorption and the facility of spin casting. In this research, the stability of PVOH thin films on PDMS substrates prepared by adsorptive spin casting was evaluated by rinsing the films with Milli-Q water immediately upon spin casting and after overnight drying. The film thickness and morphology before and after rinsing were compared as a function of PVOH degree of hydrolysis, PVOH concentration, spin rate, and rinsing method. Characterization methods include contact angle goniometry, ellipsometry, optical microscopy and atomic force microscopy. We have established that water rinsing removes the “unstable” portion of the PVOH layer. In addition, rearrangement of PVOH polymer chains takes place during the rinsing process causing further morphological changes of the thin films.

Assembly of amphiphilic homopolymers into controlled nanoscale particles

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Linear homopolymer of norbornene (NBE) derivatives equipped with hydrophilic groups were prepared by ring-opening metathesis polymerization (ROMP) and were precisely assembled into well-defined structures in alcohol solvents. Controlling ratio of hydrophobic and hydrophilic groups at the repeating monomeric unit level in these polymers resulted in determining the size of spherical particles ranging from a few nm to mm. In addition, the concentration and molecular weights of the linear polymers readily controlled the size and distribution of polymer particles. The degree of solvation with
various solvents possessing different surface tension and polarity systematically affected the final diameter and distribution of polymer particles. These observations clearly implied the important selection of proper solvent to regulate structural features of homopolymer particles. Investigating the assembly process of these types of homopolymers into uniform nanoscale particles can allow for understanding transformation of diverse linear amphiphilic polymers into well-defined structures.

**COLL 284**

**Functional dual drug-loaded dendrimer/carbon dot nanohybrids for cancer cell fluorescence imaging and enhanced therapy**

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Design of powerful nanosystems to overcome multidrug resistance (MDR) for effective chemotherapy of cancer currently remains to be a great challenge. Herein, we report the development of a poly(amidoamine) (PAMAM) dendrimer/carbon dot nanohybrid for dual drug loading to overcome the MDR and simultaneously for monitoring cancer cells via fluorescence imaging. Firstly, blue-emitting carbon dots (CDs) were synthesized using sodium citrate as a carbon source via a hydrothermal method and used as a carrier to load anticancer drug doxorubicin (DOX) via non-covalent interaction to form CDs/DOX complexes, and in parallel PAMAM dendrimers of generation 5 (G5) were covalently modified with targeting ligand cyclic arginine-glycine-aspartic (RGD) peptide and the drug efflux inhibitor D-α-tocopheryl polyethylene glycol 1000 succinate (TPGS). Then, through electrostatic interaction, functional dendrimers (G5-RGD-TPGS) were complexed with CDs/DOX complexes to form a dual drug-loaded nanohybrid system. The dual drug-loaded dendrimer/CD nanohybrids were well characterized. We show that the nanohybrids possess good colloidal stability, enable significant inhibition of cancer cells due to the presence of TPGS that can inhibit P-glycoprotein (P-gp) by decreasing ATP level and increasing ROS level, and simultaneously achieve fluorescence imaging of cancer cells in vitro due to the luminescence of CDs. In addition, the attached RGD ligands render the nanohybrid with targeting specificity to cancer cells expressing αvβ3 integrin receptors. The developed dual drug-loaded dendrimer/CD nanohybrid may be used as a promising theranostic platform to overcome MDR for enhanced chemotherapy as well as for fluorescence imaging of cancer cells.

**COLL 285**

**Investigation of ceria-nickel-containing aerogels for catalytic converter applications**

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Aerogels have physical properties that make them appealing for automotive exhaust catalysis: they are highly porous with low density and high surface area. Current catalytic converter technology uses precious metals (Pt, Pd and Rh) to oxidize CO and unburned hydrocarbons and reduce NOx. Catalytic-metal-containing aerogel can potentially be a less expensive alternative for use in catalytic converters. Prior work with nickel-alumina aerogels indicated promise for this application; the goal of including ceria is to increase oxygen storage and thereby enhance catalytic ability. Here, cerium- and nickel-containing aerogels, with an alumina backbone, are fabricated using an epoxide-assisted recipe and characterized for this application. The precursors for the aerogel, hydrated salts of aluminum chloride, cerium(III) chloride and nickel (II) nitrate, are dissolved in reagent-grade ethanol, to which propylene oxide is added. Wet gels are prepared with different molar ratios of cerium to nickel (25:75, 50:50, 75:25). Following solvent exchange, the metal-containing wet gels are processed into aerogels using a rapid supercritical extraction method, and calcined at 800 C for 24 h. Catalytic testing of the aerogels is performed using an in-house-constructed catalytic testbed under exposure to simulated automotive exhaust. As an example, 50:50 Ce:Ni Al aerogel shows nearly 100% conversion of NOx by 450 C under reducing conditions. XRD analysis indicates the presence of microcrystalline cerium(IV) and nickel species in the heat-treated aerogels, which is confirmed by SEM/EDX imaging. The presentation will include descriptions of the preparation, physical characterization (as prepared, following heat treatment and after catalytic testing), and catalytic performance of the cerium-nickel-containing aerogels.

**COLL 286**

**Boronic acid materials: Applications in glycoprotein recognition and enhanced cellular delivery**

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Cell surface glycans, glycoproteins or glycolipids, are commonly aberrant in diseases and can serve as biomarkers that facilitate diagnostics, selective cellular labeling and delivery. Boronic acids have been extensively utilized for the detection and separation for carbohydrates through reversible formation of boronate esters in the binding of diol moieties on glycans. However, the biological application of this sensing group is challenged by its relatively low binding affinity in aqueous media. Our lab designed and synthesized boronic acid materials that can enhance its avidity towards glycan through multivalent binding interaction. First, a boronic acid microplate assay for sensitive and high-throughput detection for
cancerous glycoprotein MUC1 was developed. A multivalent surface for glycoprotein recruitment and detection was achieved by immobilization of biotinylated boronic acid onto streptavidin plates. In addition, novel boronic acid lipids were synthesized and incorporated into liposome as drug delivery platform. We validated boronic acid liposome efficacy by demonstrating dose-dependent release of encapsulated hydrophobic or hydrophilic fluorophores upon titration with the polysaccharide heparin. Finally, cellular delivery and labeling was visualized by confocal microscopy through a dramatic enhancement in fluorescence signal, showcasing the prospects of boronic acid lipids for drug delivery.

COLL 287

Metal-ligand coordination for single-site catalysts on oxide surfaces

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In recent years, significant attention has been directed towards single-site metal species for catalytic reactions, particularly to take advantage of atom-utilization efficiency and unique properties of single-site atoms (Joule, 2018, 2, 1242; J. Am. Chem. Soc., 2015, 137, 10484). However, preparation methods that target well-dispersed single-site atoms with high stability during catalytic processes still need to be developed. Methods to synthesize single-site atoms usually involve wet-chemistry approaches, including defect-engineering on oxide surfaces or binding site design on zeolites, but there are also new strategies, such as single-atom alloys (Science, 2012, 335, 1209). We have recently developed a metal-organic coordination strategy to achieve single-site Pt centers on oxide surfaces (J. Catal., 2018, 365, 303). The presence of suitable ligands can alter the charge state of single metal atoms and stabilize the single-site centers against migration and agglomeration. Here we report a new set of studies where we extend the surface chemistry of this approach to a broader range of metal species, including Fe, Ru, Rh, and Ir. The metal-ligand coordination and charge transfer
are investigated by XPS by examining metal/ligand ratio and core-level shifts. Different metal centers and chemical states are explored to optimize conditions that can lead to active and stable catalysts. The gas phase catalysis of these systems is being examined.

COLL 288

Cr (VI) removal with porous Fe/C microspheres prepared from glycerol via ultrasonic spray pyrolysis

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Fe/Cs are composite materials effective for Cr(VI) removal due to synergistic adsorption and reduction effects. However, conventional Fe/C preparation involves multiple discrete steps to impregnate iron particles onto the surface of porous carbon supports, decreasing scalability and reusability. Ultrasonic spray pyrolysis (USP) is a continuous and scalable materials synthesis technique used to prepare spherical, uniformly sized particles. In this study, Fe/C composites are prepared from glycerol, a by-product of the biodiesel industry, making this study of great practical importance to apply a waste precursor for USP carbon generation. Precursor solutions containing glycerol, sulfuric acid, sodium salts, and iron salts were ultrasonically aerosolized by a nebulizer. Prepared materials were fully characterized and applied in Cr(VI) removal and regeneration tests. Carbon microspheres were developed through acid induced glycerol dehydration, polymerization, and carbonization. Variable surface morphologies and hierarchical porous structures achieved for Fe/C composites depend on selected iron and sodium salt combinations. Porosity results from iron-catalyzed carbon gasification and solid salt templating, generating carbonaceous materials dominated by meso- and macropores. Iron impregnation into carbon microspheres reaches 6.6 wt%, and the oxidation state of the iron species is tailored by changing iron and sodium salts. Fe\textsuperscript{0} was generated \textit{in situ} and impregnated into microspheres when using ferric ammonium citrate as both iron precursor and reducing agent. Potential for simultaneous nitrogen (up to 3.3 wt %) and sulfur (up to 6.3 wt%) doping is also reported. Hexavalent chromium removal efficiency of 95% at C\textsubscript{0} ≤ 20 mg/L is achieved within 2 h, attributed to meso/macropore volume that aids adsorbate diffusion and reductive iron species. Magnetic properties (up to 20 emu/g) from iron nanoparticles facilitate Fe/C separation and reuse, highlighting the performance potential of the porous Fe/C materials for heavy metal remediation.

COLL 289

Seed-mediated growth in shape-controlled synthesis of copper nanocrystals

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Copper (Cu) and Cu-based nanocrystals have received increasing attention in recent years. Due to the unique properties of Cu including high earth abundance and intrinsic conductivity, Cu nanocrystals have been regarded as promising materials for various applications such as catalysis, displays, and electronics. Mastery over the shape of nanocrystals enables control of their properties and enhancement of their performance. Among different strategies, seed-mediated growth is one of the powerful and versatile approaches for the shape-controlled synthesis of colloidal Cu nanocrystals. To date, Cu nanocrystals in various shapes have been synthesized from seeds with different compositions and structures, and the products have been used in SERS, CO$_2$ reduction, transparent conductors, and among others. We hope this brief discussion of seed-mediated growth in synthesizing Cu nanocrystals will give a general idea of nanocrystal syntheses and stimulate the devotion of more efforts into the exploration of Cu nanocrystals in both syntheses and applications.

**COLL 290**

**Simulations of grain boundaries between ordered colloidal hard sphere domains: Impurity and gravity confinement**

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New variations of grand canonical Monte Carlo simulation are implemented to investigate the properties of grain boundaries (GBs) between colloidal hard sphere ordered domains in 2d and quasi-2d conditions. We first employ the capillary fluctuation method to illustrate the dependence of GB stiffness on pressure, misorientation and inclination for 2d one-component hard sphere systems. Simulation of 2d mixtures with a range of size-mismatched impurities is then carried out to investigate the equilibrium partitioning of impurities between the GB and bulk domains, in comparison with experiment. GB stiffness depression is observed due to the presence of impurities, consistent with the Gibbs adsorption isotherm. Systems with an impurity: host diameter ratio of 4:1 show both quantitatively and qualitatively distinct behavior from other size ratios. We also investigated the GB behavior in a quasi-2d system: colloidal hard spheres confined by a gravitational potential to a thin layer (up to several monolayers) near a hard flat surface. The particles in overlayer can behave similarly to impurities in the 2d case, where the GB segregation and stiffness depression can be observed as well. Comparison with results from experimental studies will also be discussed, where possible in this work.

**COLL 291**

**Antimicrobial surface textile treatments**
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Due to the large surface area and inherent capacity to absorb moisture, textiles promote an environment for microorganism growth resulting in a range of deleterious effects to both the textile and end user. Numerous commercial and academic processes have been developed to produce antimicrobial textiles including chemical treatments or compounding biocides into fibers. These approaches typically fail due to low efficacy, poor wash durability, increased antimicrobial resistance, and cytotoxicity or sensitization. In view of this, there is a desire for novel antimicrobial textile treatments that i) demonstrate broad spectrum biocidal activity, ii) can be applied using conventional textile processing equipment, iii) exhibit durability to laundering, and iv) do not adversely affect breathability or mechanical properties of the textile. Luna Innovations has designed a waterborne covalently tethered antimicrobial textile treatment based off a highly tunable host-guest interaction on the textile surface. This crosslinkable host molecule was applied to both cotton and NYCO (50:50 cotton:nylon blend), demonstrating biocidal activity, excellent wash durability, and the ability to “recharge”. The textile treatment was shown to exhibit >5 log biocidal kill against gram negative (E. coli, P. aeruginosa) and positive (S. aureus) bacteria after up to 20 launderings. This treatment adds less than 5% weight to the fabric, allowing for similar breathability, drape, and hand compared with the untreated textile. This host-guest complex provides the ability to incorporate multiple different types of biocides and allows the biocide host-guest complex to be recharged to maintain antimicrobial activity indefinitely.

COLL 292

Novel durable, flame retardant textile treatments for nylon/cotton blends

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Military and first responder uniforms are often fabricated from nylon/cotton (NYCO) blends which are economical but suffer from significant flammability concerns. Flame resistant (FR) fabrics utilizing polyaramid (e.g. Nomex®) blends can be used instead, but they are significantly more expensive, more difficult to obtain and less durable than the NYCO materials. Historically, textile finishes based on halogenated chemical treatments have been the most cost effective FR treatments however they evolve toxic gases and do not arrest melting of the polymer under combustion conditions. The research described herein involves an investigation into a conformal polymer coating formulation that provides FR character to NYCO fabrics while ideally maintaining the desired flexibility, comfort, and physical properties for high user acceptability. A crosslinkable, phosphorous containing polyurethane formulation was applied to NYCO fabrics and evaluated for weight pickup, durability and flame resistance according to ASTM D6413. The flame resistant polyurethane coating was shown to be wash durable with no melt drip observed through 20 washes with an approximate two second
afterflame and char length of less than six inches. The weight pick-up of this durable coating system is at 30 wt. %, and research is ongoing to improve the hand, reduce the weight pick-up, and achieve wash durability out through 50 washes.

**COLL 293**

**Molecular self-assembly at surfaces: Dynamics, interactions, and design**

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In studying two-dimensional self-assemblies at interfaces, great strides have been gained in understanding how supramolecular interactions affect assembled structure to produce functional materials. However, there is a great challenge in characterizing these systems at the critical nanosecond / nanometer scales, where insight into pre-equilibrium stages and fundamental steps of self-assembly is needed to advance supramolecular design. We have studied the self-assembly of two prototypical molecular systems at the solution-graphite interface, using scanning tunneling microscopy (STM) with atomistic molecular dynamic (MD) simulations. These studies allow new insight into the fundamental steps of molecular self-assembly. The first system is an alkoxybenzonitrile that contains competing van der Waals, electrostatic, and steric interactions. STM was used to determine packing structure and to benchmark force fields. MD simulations revealed the atomistic and sub-nanosecond stages of desorption, reabsorption, and on-surface motion; this provided new insight into molecular level assembly dynamics. Second, the self-assembly of a series of π-conjugated macrocycles and their flexible precursors were compared. Peripheral functionalization with alkyl and glycol chains resulted in comparable solubility, but self-assembly can be tuned between a tight packing of aromatic cores with desorbed glycol chains or a looser packing of aromatic cores separated by interdigitated alkyl chains. While the macrocycles self-assemble immediately and spontaneously, their flexible linear precursors exhibit slower self-assembly kinetics, due to the large conformational space available. STM tip bias or aromatic co-solute reduced that conformational space and, remarkably, significantly accelerated self-assembly. The observations and from these studies provide insights into the dynamics and design rules of small molecule self-assembly.

**COLL 294**

**Interface materials on the nanoscale: Dominant media of chemical change and evolution**
The discoveries of the unique chemical properties of defects and low coordination sites of metals and the electronic properties of semiconductor transistors started the development of nanomaterials to optimize their utility as catalysts in energy conversion and chemical technologies and information storage using integrated circuits. The size and shape of nanoparticles maintained, altered, and improved their chemical activity and selectivity and the size as transistors became exponentially smaller from micron size to nanometer sizes as their numbers in the integrated circuits increased from thousands to billions. The metal nanoparticles had to be supported by oxides or polymers that contributed to their chemical behavior including the rate and selectivity of the reaction making interfaces between the support and the nanoparticles part of the chemistry of the nanocatalyst. The catalysts became interface materials with complexity that often matched the formation of complex molecules, which was the purpose of the research. In the past four decades the instruments that characterize the size, composition and bonding of the interface materials on the atomic and molecular scales developed to permit the fabrication of these complex interfaces’ reproducibly and develop protocols for their regeneration if they are deactivated. Transistor-based devices were converted to integrated circuits by connecting them to develop their use to information storage technology.

The interface device we call catalyst produced by nanoparticle and mesoporous oxide synthesis, subjected to atomic level characterization under reaction conditions. The metal nanoparticles exhibit size dependent covalent bond catalysis. The oxidemetal interfaces are active sites for acid-base catalysis. The changing oxidation states of nanoparticles with decreasing size permits their conversion from homogenous to heterogeneous catalysts. Enzymes deposited to immobilize onto glass create hybrid systems that retain remarkably high selectivity towards their substrates with high catalytic rates. Integration of the three fields of catalysis (heterogeneous, homogenous, and enzyme) becomes a future promise along with biocatalysis as the human body is an interface system of great complexity and success.

**COLL 295**

*Heats of formation of adsorbed catalytic intermediates on well-defined surfaces by single crystal adsorption calorimetry*

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David King and his group developed the first calorimeter that could measure heats of adsorption on the well-defined surfaces of single crystals with sufficient precision to reveal new understanding of surface chemistry, especially by determining the energies of adsorbed molecular fragments that are catalytic reaction intermediates and otherwise inaccessible experimentally. Since then, our group has adopted this technique and
made substantial improvements in heat detection, allowing routine measurements from 100 to 350 K with high precision (±1.3 kJ/mol in the heat for adsorbing 1% of a monolayer) and accuracy (2-3 %). We have applied it to measure the heats of formation of well-defined adsorbates on single crystal metal surfaces, including Pt(111), Ni(111) and Cu(111). Those results will be reviewed, with emphasis on the new insights they provide regarding reaction mechanisms and the differences in catalytic activity between different metals. The applications of these energies as benchmarks for assessing the energy accuracy of quantum mechanical approximations like those in density functional theory (DFT) reveal substantial errors in the relative energies of adsorbed catalytic reaction intermediates, even with the best DFT methods.

**COLL 296**

**Model interfaces constructed from ordered oxide films: From heterogeneous catalysis to electrocatalysis, photoelectrocatalysis, and organic-oxide hybrid materials**

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Model system based on ordered oxide films have been developed by Hajo Freund and coworkers over a period of 30 years and have been used in many pioneering model catalytic studies. This contribution provides an overview over recent work by the presenter’s group making use of the same concept. Besides ‘conventional’ model studies of solid/gas reactions, the focus is on ‘unconventional’ model studies involving solid/liquid, electrochemical, and hybrid interfaces. Typical supported model catalysts, i.e., Pt and Pd NPs on ordered alumina supports, were used to study hydrogen release from so called Liquid Organic Hydrogen Carriers (LOHCs).[1] LOHCs are organic molecules which can be reversibly (de)hydrogenated. They allow storing hydrogen at room temperature and pressure in form of a rechargeable liquid fuel that can be easily transported. Using model catalytic studies, the mechanism of LOHC dehydrogenation and particle size effects could be explored. The same type of model catalysts, i.e., Pd NPs on alumina thin films, was used to build model systems for so-called SCILLs (Solid Catalysts with Ionic Liquid Layer).[2,3] Ionic Liquids (ILs) are low-melting-point salts. In the SCILL concept, they are employed as catalytic modifiers to enhance the selectivity of hydrogenation catalysts. The underlying operation principles were explored using the model catalysis approach. Recently, we have shown that the same type of model approach can also be used to construct complex model electrocatalysts.[4,5] We prepared atomically-defined oxide-based electrodes under surface science conditions and studied their properties in liquid electrolytes. When loaded with noble metal NPs, such systems allow studying particle size effects and metal-support interactions at a great level of detail. Finally, we show that ordered oxide films can also be used to build atomically-defined model systems for organic-oxide interfaces.[6] Such systems can be studied both in ultrahigh vacuum and in liquid electrolytes under potential control, with the idea to build model interfaces for solar cells, molecular electronics or photochemical devices.
COLL 297

Vinyl acetate formation pathways and selectivity on model metal and alloy catalyst surfaces

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Surface reaction pathways are explored on model single crystal catalyst surfaces using a combination of surface science experiments in ultrahigh vacuum, in-situ monitoring of the surface intermediates during reaction, and by using density functional theory (DFT) calculations. This approach enables detailed reaction pathways to be obtained and is illustrated using palladium- and palladium-gold alloy catalyzed synthesis of vinyl acetate monomer (VAM). It is shown that vinyl acetate is formed on a Pd(111) model catalyst via the so-called Samanos pathway, where reaction is initiated by coupling between ethylene and surface acetate species to form an acetoxyethyl intermediate that decomposes by β-hydride elimination to form VAM. The way in which adsorbate coverage affects both reactivity and selectivity is discussed. Gold-palladium alloys are found to improve the selectivity of the commercial catalyst. The origins of the catalytic selectivity and activity of the alloys are also investigated by exploring reactions on well-characterized Au/Pd(111) and Au/Pd(100) model alloys.

COLL 298

Polarons on TiO$_2$ and their affinity for water

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Small electron polarons associated with bridging oxygen vacancies have been shown to be present on TiO$_2$(110). Above 17 K they hop around the vacancies. Here we look at the interaction between these polarons and water. Water-oxide surfaces are ubiquitous in nature and of widespread importance to phenomena like corrosion as well as contemporary industrial challenges such as energy production through water splitting. So far a reasonably robust understanding of the structure of such interfaces under certain conditions has been obtained. Considerably less is known about how overlayer water modifies the inherent reactivity of oxide surfaces. Here we address this issue experimentally for rutile TiO$_2$(110) using scanning tunneling microscopy and photoemission, with complementary density functional theory calculations. Through detailed studies of adsorbed water nanoclusters and continuous water overlayers, we determine that excess electrons in TiO$_2$ are attracted to the top surface layer by water molecules. Measurements on methanol show similar behavior. Our results suggest that adsorbate-induced surface segregation of polarons could be a general phenomenon for technologically relevant oxide materials, with consequences for surface chemistry and the associated catalytic activity.

COLL 299
Bioinspired materials synthesis in microenvironments formed by liquid-liquid phase separation

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Biological cells are highly organized with numerous subcellular compartments, many of which lack membranous boundaries. We are developing simple experimental models for these membraneless organelles based on liquid-liquid phase separation, which is a common phenomenon in aqueous solutions of polyelectrolytes and other macromolecules. Solute such as ions, small molecules, and biopolymers can become compartmentalized by partitioning between the phases. This generates microenvironments that can impact reaction locations, rates, and outcomes. For example, compartmentalization of catalysts and/or mineralization precursors in polymer-rich droplets can control formation of bioinspired organic/inorganic composite materials.

COLL 300

Nature-inspired elastic capsules, tubes and hairy surfaces

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Natural structures such as eggs, embryos, plant seeds, vegetables like the onion, and body parts like the spinal disc, all have multiple concentric layers surrounding a central core. Each layer typically has a unique composition and thereby a distinct function. The synthesis (morphogenesis) of these structures in nature typically proceeds in an “inside-out” fashion, where a core is formed initially, followed by a first shell and then additional shells.

Taking inspiration from the above, we have developed an inside-out technique to synthesize a range of soft materials. First, we have created “onion-like” polymeric capsules with multiple concentric shells surrounding a gelled core. Each polymer shell is formed by free-radical polymerization. A given shell grows outward from the surface of the previous shell; thus, the shell thickness steadily increases with time and can be controlled. Using this technique, we can juxtapose widely different polymers next to each other in a capsule. The resulting capsules exhibit a range of unusual properties. One specific property to highlight is the ability of capsules to rapidly swell due to gas evolved from a reaction in the core; such swelling can be violent enough to eject the core.

Multilayered structures in nature also exist in other geometries. Our blood vessels are examples of multilayered tubes, while many tissues in our body have outer layers of hairs called villi and microvilli. We have extended our inside-out technique to cylindrical and planar geometries to create polymeric multilayered tubes and hairy surfaces. The multilayered tubes exhibit spontaneous changes in tube diameter in response to the
properties of the flowing liquid, which is reminiscent of blood vessels. The hairy surfaces absorb solutes much more efficiently than a bare surface, akin to the villi-covered surfaces of the gastrointestinal tract.

**COLL 301**

**Thermophoretic manipulation of biomaterials mechanical properties in microfluidics**

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Optimisation of cell material interactions is important for tissue engineering and biomedical applications. Applications such as tissue repair and wound healing could be greatly improved using 3D scaffolds where cells are directed in specified areas of interest. Biomaterials exhibiting a gradient of mechanical properties can be used to regulate cell behaviour which is mainly dependent upon the elasticity of the substrate. However, the possibility to create these materials is still limited especially at the micron scale. By carefully imposing and controlling temperature gradients across a microfluidic channel and exploiting the phenomenon of thermophoresis, we demonstrate the generation of gradients with tuneable properties in colloidal systems. Particularly, a microfluidic device consisted of a main microchannel and two side channels acting as hot and cold thermal sources are used to apply the temperature gradient and fabricate biocompatible gellan gum hydrogels exhibiting stiffness gradients. Moreover, we effectively control the stiffness gradient of the biomaterials by regulating the temperature difference across the device and altering the concentration of the polymer. Using Atomic Force Microscopy we characterise the biomaterials by evaluating locally the Young’s modulus across the 600 μm width of the hydrogels, obtaining values ranging from 20 to 100 kPa. Furthermore, we monitored cell behaviour over time by seeding MC3T3 osteoblasts on the surface of the biomaterial. Cell migration and mineralisation are observed on the surface of the material at different stiffness areas and time points. Finally, we evaluated cell activity throughout the gradient which gave us valuable information for the design of future 3D scaffolds.
One of the primary limitations in drug discovery and toxicology research is the lack of good model systems between the single cell level and animal or human systems. This is especially true for neurodegenerative diseases such as ALS, Alzheimer’s, and spinal cord injury. In addition, with the banning of animals for toxicology testing in many industries body-on-a-chip systems to replace animals with human mimics is essential for product development and safety testing. Our research focus is on the establishment of functional in vitro systems to address this deficit where we seek to create organs and subsystems to model motor control, muscle function, myelination and cognitive function, as well as cardiac subsystems. The idea is to integrate microsystems fabrication technology and surface modifications with protein and cellular components, for initiating and maintaining self-assembly and growth into biologically, mechanically and electronically interactive functional multi-component systems. We have also integrated bioprinting of cells on controlled interfaces for cellular engineering of more advanced systems. Our advances in culturing adult rat, mouse and human mammalian spinal cord, hippocampal neurons, muscle and cardiac cells in a defined serum-free medium,
suggest outstanding potential for answering questions related to maturation, aging, neurodegeneration and injury. We are using this ability to manipulate the biological systems and integrate it with silicon-based systems to create cell-based sensors for high content drug discovery. We are also using what we learn for a more fundamental understanding of cellular development, protein adsorption and neuronal regeneration. Examples will be given of some of the more advanced human-on-a-chip systems being developed.

**COLL 303**

**Designing biomimetic interfaces for blood-contacting biomaterials: New insights from single-molecule microscopy**

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Understanding of nonspecific protein adsorption mechanisms at solid-liquid interfaces is critical to rational design of surfaces for biomedical and industrial applications, such as medical devices, drug delivery carriers, marine coating, and biosensors. For blood-contacting medical devices, for example, contact with blood results in rapid nonspecific protein adsorption. This protein layer may initiate blood clotting by promoting platelet adhesion, activation, and aggregation. Therefore, materials are often engineered to enhance resistance to nonspecific protein adsorption through surface modification. Optimizing the design of blood compatible surfaces requires a detailed understanding of protein-surface interactions.

Protein interaction with solid interfaces is a result of transport, adsorption, desorption, and reaction processes. Individual protein surface interactions can result in reversible or irreversible binding, and some proteins may also undergo conformational changes after adsorption. Constructing a detailed model of protein-surface interactions requires that these phenomena be observable at the single-molecule level.

We have studied the dynamics of protein adsorption on synthetic surfaces including polyelectrolyte multilayers, glycocalyx-like surface coatings, and PEG surfaces. We have used single-molecule tracking to measure a large number of single protein trajectories (>\(10^4\) in each experiment) to explicitly visualize the processes of adsorption and desorption of albumin and fibrinogen on these model surfaces. These direct experimental observations inform a mathematical model that describes protein adsorption and desorption and possible denaturation. This detailed characterization of protein-surface interactions can be used to design improved glycocalyx mimetic surfaces for blood-contacting biomaterials.
Studying the response of human macrophage-like cells to surface chemistry with diazonium-modified polystyrene substrates

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Macrophages help direct the tissue repair process with their ability to polarize, or change their phenotype, throughout the wound healing process. During the early stages, macrophages take on a pro-inflammatory state to promote revascularization of the wounded tissue while at later stages, they shift towards an anti-inflammatory state to initiate wound healing and repair. Since implanting a biomaterial creates a wound,
macrophages are recruited to the implant site to direct the repair process where they interact with the implant’s surface. The macrophages can either promote normal repair or foreign body reactions (FBR). Although many hydrophobic materials tend to elicit FBRs, there is little understanding of how the surface properties of the implant materials impact macrophage-mediated FBR. Some studies have shown that altering wettability alters macrophage polarization, but results between studies are inconsistent because wettability depends on both surface chemistry and topography. To better understand the effect of surface properties on macrophage polarization, surfaces with well-characterized properties are required. In this study, polystyrene substrates were functionalized with primary amine (NH$_2$), carboxylic acid (COOH) or phosphonic acid (PO$_3$H$_2$) groups using diazonium chemistry modifications. Their surface properties, including surface composition, wettability and topography, were characterized with techniques including X-ray photoelectron spectroscopy, water contact angle and atomic force microscopy. Then, THP-1 human macrophage-like cells were cultured on the surfaces, and their gene expression, cytokine production and adhesion were quantified after 4, 24, and 48h. All surfaces promoted similar macrophage adhesion and spreading regardless of their surface chemistry and culture time. However, the COOH functionalized surfaces led to significant increases in the anti-inflammatory cytokine, IL-10, after 48h compared to tissue culture polystyrene. This suggests that COOH groups could be applied to implant surfaces to promote a wound-healing phenotype in macrophages and improve implant integration.

Functional microgels for decoration of biointerfaces

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Aqueous microgels exhibit unique properties like high chemical functionality, reversible deformability, surface activity, and stimuli-responsiveness. Microgels can display sensitivity to temperature, pH, light, ionic strength and other stimuli. Applying different synthesis methods, it is possible to modulate their size and size distribution, chemical functionality, surface charge, swelling degree, and colloidal stability. Functional microgels can be used as building blocks for the preparation of well-ordered nanostructured materials of different dimensions and complexity. The functionalization of microgels surface plays crucial role to ensure adhesion to different surfaces and efficient interactions with biological tissues. Different chemical functionalities can be efficiently incorporated into the microgel surface during precipitation polymerization process using macromonomer approach. Amphiphilic poly(ethylene glycol)- or poly(glycidol)-based macromonomers exhibit surface-active properties and form functional layer on the microgel surface during microgel nucleation and growth. This technology allows flexible decoration of microgels surface with dyes, sugars or antibacterial molecules.

Functionalized microgels can be used as colloidal building blocks for the decoration of surfaces. Compact microgel films were fabricated on different surfaces by spin-coating
or dip-coating processes. Highly functional and stimuli-responsive microgel arrays attached to glass surface were successfully fabricated by microcontact printing process using wrinkled PDMS templates. Microgels influence size, speed and dynamics of focal adhesions as well as cell motility forcing cells to move along highly directional trajectories. The modulation of microgel swelling degree and mechanical properties by the temperature or spacing serves as an effective tool for the regulation of cell motility. Aqueous microgels are versatile colloidal building blocks for the decoration of biointerfaces and fabrication of antibacterial and regenerative implant coatings or synthetic biofilms.

**COLL 306**

**Phase-separated liposomes for enhanced chemotherapeutic delivery**

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Chemotherapeutics are plagued by dose-limiting toxicity. Large, often harmful, doses are required to achieve therapeutic effects due to inefficient delivery mechanisms. Liposomes and other nanoparticles help to increase localization of drugs within tumor tissue, yet the nanoparticle itself can act as a barrier to drug release into tumor cells. Therefore, delivery remains an inefficient process. Cationic molecules, which are able to permeabilize cellular membranes, have been incorporated into liposomes to increase the efficiency of drug delivery to the cytoplasm (A). However, toxicity associated with high concentrations of cationic lipids is a key limitation of this strategy. Toward overcoming this limitation, we have employed membrane phase separation to locally concentrate cationic lipids on the surfaces of liposomes. This novel approach reduces the overall concentration of cationic lipids required for efficient delivery. Specifically, we demonstrate that concentrating the cationic lipid 1,2-dioleoyl-3-trimethylammonium-propane (DOTAP) within liquid disordered membrane domains substantially increases in vitro delivery of the chemotherapeutic doxorubicin (DOX). Phase-separated liposomes (B) that concentrate DOTAP in lipid domains are 4 times more toxic to HeLa cells compared to homogenous liposomes (C), which contain an even distribution of DOTAP over the membrane surface (D). These data demonstrate that membrane phase separation can enhance delivery of chemotherapeutics by locally concentrating cationic lipids. More broadly, we anticipate that membrane phase-separation will provide a useful tool for tuning the interactions between liposomes and cells, a key step toward overcoming multiple barriers to therapeutic delivery.
Enhanced delivery of quantum dots and gold nanocrystals to live cells

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Developing multimodal imaging platforms, based on colloidal nanocrystals such as luminescent quantum dots and plasmonic nanomaterials, to track live cells and tissue has been pursued by several groups. A major challenge is the lack of adequate and effective strategies to deliver these nanocrystals into the cytoplasm of live cells. We have designed a set of high affinity hydrophilic polymer ligands and tested them for the coating of various inorganic nanocrystals (e.g., luminescent quantum dots and Au nanocolloids). We have further introduced additional reactive groups for coupling the polymer-coated nanocrystals to specific cell targeting peptides or/and NMR-active labels.

We report on the use of an anti-microbial peptide to promote the uptake of QDs, AuNPs and AuNRs into mammalian cells. Using fluorescence microscopy experiments, we found that incubation with these conjugates yielded nanocrystal staining throughout the cell volumes. Furthermore, uptake persisted under endocytosis inhibition conditions, such as incubation at low temperature and in the presence of hypertonic sucrose solution. These findings were further complemented with confocal microscopy and flow cytometry measurements. Overall, the imaging data support the hypothesis of physical translocation of these conjugates through the membrane rather than endocytosis.
Analytical ultracentrifugation of nanocrystals and fullerenes for biolabelling

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Analytical Ultracentrifugation (AUC) has long been used to characterise the molecular weight of biomolecules and can be used to determine binding coefficients in some cases. A fundamental challenge has been to incorporate shape and inhomogeneous density of biological molecules into the equations for sedimentation. In particular, there is a concern as to whether the classical Stokes-Einstein-Sutherland (SES) equation is valid, which assumes non-slip boundary conditions. We have studied the sedimentation of both fullerenes and CdSe nanocrystals to resolve these uncertainties. We will show that the SES equation appears to be valid for solutes down to 1nm in diameter. Importantly we resolve the density and thickness of the organic ligands on the CdSe which enables these particles to be used in biomolecule labelling experiments.

Gold nanoparticles for specific binding and internalization in cells

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Colloidal Gold nanostructures are promising materials for biomedical applications because of their good biocompatibility and their unique optical properties. Here we used different kinds of Gold nanostructures such as Gold nanoparticles (AuNPs), Gold nanorods (AuNRs), and small Gold nanoclusters (AuNCs) to investigate their interaction with cells. Besides size variation we functionalized their surface with aptamers for a specific interaction with BaF3 cells for different biomedical applications. By using different analytical and optical methods (ICP-MS, confocal spectroscopy, FLIM) we could show that after a short incubation time the particles are already binding to the cells and are internalized by receptor-mediated endocytosis.

Gold nanoparticle-cell interactions

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In this presentation I will discuss the recent developments in my group regarding the interactions of gold nanoparticles capped with different types of ligands and cells. Main points will include how the morphology of the nanoparticles and the surface ligands
influence the interactions of nanoparticles with cells. The presentation will also explore
the customization of the ligand shell to design nanoparticles with multitasking roles.

COLL 311

Plasmonic nanoparticle assemblies for real-time reaction monitoring

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Organizing nanoparticles into supercrystals comprising multiple structures remains
challenging. Here, we achieve one assembly with dual structures for Ag polyhedral
building blocks, comprising truncated cubes, cuboctahedra, truncated octahedra, and
cubes. We create two micro-environments in a solvent evaporation-driven assembly
system: one at the drying front and one at the air/water interface. Dynamic solvent flow
concentrates the polyhedra at the drying front, generating hard particle behaviors and
leading to morphology-dependent densest-packed bulk supercrystals. In addition,
monolayers of nanoparticles adsorb at the air/liquid interface to minimize the air/liquid
interfacial energy. Subsequent solvent evaporation gives rise to various structurally
diverse dual-structure supercrystals. The topmost monolayers feature distinct open
crystal structures with significantly lower packing densities than their densest-packed
supercrystals. We further highlight a 3.3-fold synergistic enhancement of surface-
enhanced Raman scattering efficiency arising from these dual-structure supercrystals
as compared to a uniform one.

COLL 312

Surface modification strategies for interfacing metal nanoparticles with biological
systems

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Metal nanoparticles have been extensively explored for imaging, photothermal
therapeutic, and drug delivery applications, due to their tunable photophysical properties
accessed by feasible syntheses that allow for control over their sizes and morphologies.
However, in order to design efficient nanoplatforms for these applications, the
relationship between physicochemical properties (e.g. surface chemistry, size, form,
charge) of such colloidal particles and their interactions with biological entities must be
understood in detail. To improve the aqueous stability and decrease the undesirable
nonspecific protein adsorption to NPs surfaces, different polymers together with the
well-established poly(ethylene glycol) (PEG) ligand, have been developed and used as
coating materials to construct hybrid nanostructures. However, recent research has
indicated that PEGylated biomaterials could lose stealth functions and undergo
accelerated blood clearance by mononuclear phagocyte system. Therefore, the
development of alternative coating materials that provide highly colloidal stable gold
nanoparticles with low affinity for biomolecules present in physiological media and that
impair functionalizable groups and evade the recognition by the immune system is
highly desirable. The results presented will include surface chemistries approaches
based on the use of active antifouling glycans [1], silica monolayers [2] and
supramolecular chemistry [3] to increase stealth functions and to modulate cellular
interactions.

COLL 313

Nanoparticle-cell interactions: Implications on nanomedicine

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The micro- and nanoparticles (NPs) are attractive materials for a wide range of
applications. For the safety use of NPs in medicine, it is crucial to evaluate and
understand how the different physicochemical properties of NPs modulate the interact
with cells and environment. Indeed, NPs–cell interactions play an important role in the
targeted delivery of nanomedicines to a desired side, in the fate and degradations of
NPs, in nanosafety and in others. Therefore, a deeper understanding in these areas will
be important for the synthesis of new materials with desired properties for specific
applications. Here, we will discuss and provide an overview of different approached
used to quantify nanoparticle cell interactions, and several strategies will be presented
in form of examples.

COLL 314

Novel concepts in plasmonics

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Plasmon resonances with their dramatically enhanced cross sections for light harvesting
have found numerous applications in a variety of applications such as single particle
spectroscopies, chemical and biosensing, subwavelength waveguiding and optical
devices, and photocatalysis. In this talk I will discuss recent progress from my group.
The topics include aluminum plasmonics, molecular plasmonics, plasmon-enhanced
photodetection, plasmon-enhanced nonlinear optics, plasmon-induced hot carrier
generation, and plasmon-enhanced photocatalysis.

COLL 315

Probing molecule-plasmon dynamics with ultrafast SERS
An exciting development in the plasmonic nanomaterials field is the discovery of their ability to mediate a broad variety of chemical reactions. To achieve the full potential of these materials as solar-driven photocatalysts, a mechanistic understanding of plasmon-driven chemistry is required for further optimization. Here we describe our use of ultrafast surface-enhanced Raman spectroscopy (SERS) to probe molecule-plasmon dynamics on the ultrafast timescale of nuclear motion and chemical reactivity. We examine contributions of plasmon-derived hot carriers, localized heating, and energy transfer to molecular photochemistry on the ultrafast timescale, and discuss implications of these processes for the plasmonic photocatalysis field.

COLL 316

Shifting the plasmon resonance of gold nanoparticles with incident light intensities as low as those encountered in ordinary UV-visible spectroscopy

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Atwater and coworkers, recently showed that when a metal nanoparticle residing near a bulk conducting surface is illuminated with light near but slight off its plasmon resonance wavelength, the particle will either lose or gain electrons to or from the bulk conductor so as to shift its plasmon resonance wavelength to be in better accord with that of the illuminating light. This comes about on account of the fact that on-resonance the entropy change accompanying the light absorption process is increased, primarily as a result of temperature increases brought about through non-radiative processes returning the nanoparticle to its ground plasmonic state. We have fabricated a series of metal-particle/thin semiconductor film/metal-film devices that show that for a well-engineered device even the low intensities a sample encounters during the measurement of a routine UV-Visible spectrum is able to alter the nanoparticles’ electron charge density thereby measurably shifting the location of the system’s plasmonic absorption.

COLL 317

Charge injection properties in plasmonic nanocomposites and thin films

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Sensitizing the surface of metal oxide semiconductors with plasmonic metal nanoparticles has been a prominent area of research in recent years. The platelet
geometry of Ag is particularly attractive for maximizing absorption in the visible region. The tunable nature of the surface plasmon resonance (SPR) in the visible region, via changes in the particle size and shape of the metal nanoparticle, is the driving force behind its use in improving visible light harvesting for improved photodegradation efficiency. The introduction of anisotropic Ag nanoplatelets to the surface of TiO$_2$ shows remarkable activity under visible irradiation offering a potential solution to the band gap limitations of TiO$_2$. We report the growth of anisotropic Ag on the surface of electrospun TiO$_2$ nanofibers. These nanocomposites exhibited a two fold increase in the degradation rate of methylene blue under solar irradiation, in comparison to raw TiO$_2$ nanofibers. These results were further supported and explained by computational electromagnetic modeling and transient infrared spectroscopy studies, which demonstrated the enhanced absorption and charge injection capabilities of the nanocomposites, respectively. Finally, new results in the charge injection properties of functionalized aluminum nanohole arrays will also be presented.

**COLL 318**

**Nanotechnology enables hot gold nanorods to kill cancer cells and to stop alive sick cells from migrating to other places in the body**

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Cancer kills many people after several years of suffering and after using a great deal of different unsuccessful treatments, like surgery, chemical and/or radiation treatments. The field of Nanotechnology showed us how different materials acquire so many different properties when their size is reduced to the nanometer scale. Gold nanoparticles having rod shape of nanometer size and a length: width ratio of 3:1 can absorb near infrared light (to which our body is transparent) and convert it into heat. If solution containing gold nanorods is injected into a cancer lump and exposed to near infrared light, the hot solution (resulting from the gold nanorods upon absorbing the near infra-red light) melts the cancer cells leading to their death. This was demonstrated by our group in the photo-thermal destruction and destroying cancer cells in solution and in cancer lumps in small and large animals. Normally, some of the cancer cells that do not die are able to migrate to other parts of the body away from the location of their initial formation spot until they are located in a sensitive part of the body that leads to the cancer patient death. Thus, most of the cancer patients die from cancer after the cancer cells migrate by a process called metastasis to a more sensitive part of the body.

Very recently, however, we discovered that in our photo-thermal treatment, while treating cancer cells in the first cancer location with hot gold nano-rods, the cancer cell legs and arms and the motion proteins are photo-thermally destroyed. This makes it difficult for the cancer cells to migrate to a new more important functional locations in the body. This treatment is thus effective in stopping cancer cell migration through the patient body and increases the success rate of the patient recovery.
Light years: Combined optical and environmental electron microscopy to visualize photonic processes with atomic-scale resolution

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Pearl Jam’s hit, “The Light Years,” declares “We were but stones, light made us stars.” Bringing light to the transmission electron microscope (TEM) promises to transform our understanding of materials, enabling both direct observation of light-mediated processes and detection of optical emission with atomic scale resolution. To help achieve this goal, my lab is developing capabilities for concurrent optical and electron microscopy within an environmental TEM. This presentation will describe our efforts to visualize a variety of photochemical processes in situ with nanometer-to-atomic scale resolution. We focus in particular on i) observing photocatalytic phase transitions in nanoparticles; ii) detecting quantum light emission from two-dimensional materials; and iii) designing electron-stable fluorescent tags. First, under controlled hydrogen pressures, temperatures, and optical illumination conditions, we study the study the hydrogenation and dehydrogenation of Pd with sub-2-nm spatial resolution and millisecond time resolution. Particles of different sizes, shapes, and crystallinities exhibit distinct thermodynamic and kinetic properties, highlighting several important design principles for next-generation photocatalysts and energy-storage devices. Secondly, we use scanning transmission electron microscopy and cathodoluminescence spectroscopy to investigate color centers in two-dimensional hexagonal boron nitride, a wide bandgap material capable of room-temperature, high-brightness visible quantum emission. We find that sharp, single-photon emission peaks are usually associated with regions of high strain and grain boundaries, facilitating design of next-generation two-dimensional materials and devices. Finally, we describe the design and characterization of nanoparticles that serve as bright emitters within an electron microscope for concurrent optical and electron spectroscopy. In biological specimens, these nanoparticles could enable identification of molecules or proteins with sub-10nm resolution, while simultaneously revealing the ultrastructure of the cell.

Matter in motion by liquid cell TEM: Phase transitions, diffusion, collisions, and growth mechanisms

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Amphiphilic small molecules and polymers form commonplace nanoscale macromolecular compartments and bilayers, and as such are truly essential components in all cells and in many cellular processes. The nature of these architectures, including their formation, phase changes, and stimuli-response behaviors
are necessary for the most basic functions of life, and over the past half-century, these natural micellar structures have inspired a vast diversity of industrial products, from biomedicines to detergents, lubricants and coatings. The importance of these materials and their ubiquity, have made them the subject of intense investigation regarding their nanoscale dynamics with increasing interest in obtaining sufficient temporal and spatial resolution to directly observe nanoscale processes. However, the vast majority of experimental methods involve either bulk-averaging techniques including light, neutron and X-ray scattering, or are static in nature including even the most advanced cryogenic transmission electron microscopy techniques. Here, we describe in situ liquid cell transmission electron microscopy (LCTEM) for the direct observation of the evolution of individual amphiphilic block copolymer micellar nanoparticles in solution, in real time with nanometer spatial resolution. In addition, we explore other organic materials, and hybrid materials for the formation and growth in solutions including aqueous and organic solvents.

Coll 321

3D structure study of colloidal nanocrystals using liquid phase TEM

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Three dimensional (3D) atomic structures of materials govern the physical and catalytic properties of materials. As the material dimension becomes nanometer-scale, 3D structures of colloidal nanocrystals typically deviate from the lattice structures measured and expected in their bulk counterparts. This is presumably because of the dominance of surface dangling bonds, defects, and dislocations within the volume of nanocrystals. To understand these unique structural features of nanocrystal, a method that can precisely determine the positions of the individual atoms is required. We introduce our experimental efforts using a combination of new techniques including graphene liquid cell for in situ TEM, aberration-corrected TEM, structure analysis algorithm, and 3D
strain measurement. We apply it to determine the 3D atomic arrangements of different types of nanocrystals in solution. Our high-resolution 3D density maps and fitted atomic models show crystal structures of individual nanocrystals with structural degeneracies, including single crystalline, polycrystalline, distorted structures, and a dislocation. We also discuss the extent of this new analytical method regarding types and dimensions of materials systems which require unprecedented structural information in native conditions.

**COLL 322**

*In situ* look at interfacial controls over nucleation and growth of nanostructured materials

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In the classical picture of crystalization, nucleation and growth occur via monomer-by-monomer addition, first to sub-critical clusters that form via thermal fluctuations and then to kink sites on the surfaces of super-critical particles. In contrast, recent observations of crystallizing systems have revealed a rich set of “hierarchical” pathways involving higher-order species. To understand the thermodynamic and kinetic sources of such pathways, we are using *in situ* TEM and AFM to observe crystallization of calcium carbonate, iron oxide and aluminum oxide. Here we present results that highlight the importance of interfaces in pathway selection. We observed sub-critical clusters and their transition to stable nuclei using high-speed, atomically-resolved AFM to image formation of aluminum hydroxide films at the mica-water interface. We find hydrolyzed Al-precursor species are concentrated by the negative mica surface and that fluctuating aluminum hydroxide clusters form within this precursor-rich region. The cluster populations drop off exponentially with size and subcritical clusters show dynamic fluctuations, consistent with classical predictions, but nucleation of stable islands is not a rare event as expected in the classical picture. In situ TEM studies show all four common phases of calcium carbonate can form directly, but crystalline phases can also form indirectly from amorphous precursors, which provide an interface for nucleation of the crystals that then grow by consuming the precursor. These results are consistent with the classical picture in which the high supersaturation needed to overcome the free energy barrier to calcite formation opens the path to all phases, while surfaces provide a low energy barrier. Cryo-, ex situ, and high temperature in situ (S)TEM on the iron oxide system shows that heating of ferrihydrite (Fh) precursors in pure solutions produces well faceted hematite (Hm), but addition of oxalate ligands leads to a hierarchical pathway. First, Hm nanoparticles nucleate sporadically on Fh, but the adsorption of oxalate
inhibits their growth and causes subsequent particles to form within about 1 nm of existing Hm surfaces. These then assemble to form spindle-shaped aggregates of coaligned particles with a constant, reproducible shape. These findings reveal the extent to which crystallization in these systems can be understood from the standpoint of classical descriptions and delineate aspects that require alternative descriptions.

**COLL 323**

**Investigating magnetic nanoparticle interactions with Cryo-TEM**

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The effective application of magnetic nanoparticles *in-vivo* requires a complete understanding of their behavior and interactions in differing environments. Superparamagnetic nanoparticles are promising candidates for biomedical applications due to their high susceptibility and zero coercivity, by definition. In the presence of an applied magnetic field superparamagnetic nanoparticles are known to form chains, where the giant coherent spins align with the direction of the field. In the absence of an applied field superparamagnetic nanoparticles have been shown to form rings, or flux closure loops; however, these are typically discovered upon drying and do not necessarily represent behavior in solution. Recent analysis using small angle neutron scattering (SANS) showed that superparamagnetic Fe₃O₄ nanoparticles coated in a hydrophilic polymer exist as dimers or higher order aggregates in solution. To further investigate this we performed cryogenic transmission electron microscopy (cryo-TEM) experiments to capture a snapshot of the behavior in solution. We show that dimers and longer chain length structures do exist, confirming the observation in SANS. Furthermore, we observe unique arrangements of the nanoparticles which are not captured in scattering experiments, indicating cryo-TEM is a powerful tool for investigating nanoparticle interactions in solution.

**COLL 324**

**Gentle etching of metal from polymeric three-dimensional structures: Making scanning electron microscopy a non-destructive technique**

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A gentle chemical etching process is reported that can be used to remove gold and palladium from complex three-dimensional (3D) nano-scale structures. Scanning electron microscopy (SEM) is widely used to image and structurally characterize nano-scale structures and devices. Non-conductive structures, such as polymeric devices,
must be sputter-coated with metal to avoid surface charging during SEM imaging. Metallization changes the chemical, optical, mechanical, electrical, and thermal properties of such structures, effectively making SEM imaging a destructive technique. Etchants based on iodine dissolved in a chloride-rich eutectic can oxidize noble metals, and a related process has been reported for restoring macroscopic archeological samples after SEM imaging. This approach was modified further in the current work so it could be used to remove metal after SEM imaging from 3D polymeric nano-scale structures, including those with topologically complex internal structure. The method is illustrated by removing metal from photonic crystals fabricated by multi-photon lithography. Optical characterization after etching shows that the unique optical properties of the nanophotonic device were completely restored. Additional SEM imaging shows that the etching process does not perceptibly alter microstructures. This work demonstrates that the modified etching process can be used to remove metal from polymeric 3D micro- and nano-scale structures with complex internal structure, effectively making SEM a non-destructive technique.
Scanning electron microscopy (SEM) images of 3D polymeric microstructures before and after metal etching. The structures show no evidence of distortion caused by the etching process. Even artefacts created during fabrication, like those circled in red, remain clearly visible after etching.
Two types of water on free-standing reduced graphene oxide revealed by neutron scattering

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Reduced graphene oxide (rGO) has potential applications in various areas due to its extraordinary properties and facile large-scale production. Water on rGO plays a crucial role for both the preparation and application, however, its microscopic picture is still ambiguous. Herein, we studied the dynamics and temperature dependence of water on single-layer free-standing rGO using neutron scattering. Neutron diffraction measurements verify hexagonal ice forms on rGO with the melting temperature slightly lower than 273 K, whereas elastic incoherent neutron scattering data show diffusive behavior of water at ~200 K. These results suggest that two types of water coexist on rGO below 273 K. In addition, water on free-standing rGO moves slower than bulk water at 280 K, and conducts subdiffusion. These investigations reveal the influence of rGO on its surface water, and may shed light on the study on water confined in graphitic surface and the application of graphene-based materials.
range from 0.45 to 1.75 Å$^{-1}$ for rGO+(0.58)H$_2$O with the instrumental resolution times of 1 ns (blue stars) and 60 ps (red squares), and for dry rGO (black circles) with the instrumental resolution times of 40 ps as comparison. A clear harmonic to anharmonic transition occurs around 210 K when the time resolution (Δt) is 1 ns while this transition shifts to 230 K when Δt is reduced to 60ps. This should arise from the non-freezing water, the relaxation time of which is temperature-dependent and decreases from 1 ns to 60 ps when the temperature increases from 210 K to 230K. In addition to this resolution-dependent transition, the surface water also presents a sharp transition around 270 K, and more importantly the associated transition temperature is resolution independent. This 270K transition should be simply first-order phase transition between bulk-like water and ice.

**COLL 326**

Interface and dynamic indentation of crosslinked polyester films

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The objective of this study was to analyze the mechanical response of nano-indentation loading on surfaces and interfaces of polymer films both linear and cross-linked. Polymer films on nano-indentation show confinement effect on their modulus and hardness. Reduced modulus and hardness in polyester and polycarbonate show strain softening that is associated polymer chain flexibility. The spatial constraints imposed to the plastic flow of the interface layer by the rigid indenter and substrate surfaces produce a dynamic effect, demonstrated by the loading rate dependence of the deformation response. In nano-indentation of cross-linked polymers, entanglements physical and chemical affect reduced modulus and hardness dependence on strain. Strain softening and strain hardening as well as dynamic frictional response are applied to indented polymer films consisting of surface, intermediate, and interface layers. A model of wear is formulated which considers coefficient of friction, dependent on hardness to reduced modulus of matrix and nano-filler, concentration of nano-filler and interaction factor between matrix and nano-filler.

**COLL 327**

Complexity in metal-organic redox assembly at surfaces: Bimetallic sites and redox isomer surface structures

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Single-site transition metal centers at surfaces are of growing interest in developing new chemical functionality. We study a redox assembly approach using a metal-organic coordination strategy to achieve greater complexity. Here, we report new results in which some structural order is exchanged for variation in electronic character of the metal sites. A tetrazine with two electron withdrawing pyrimidinyl substituents was co-deposited with platinum metal on the Au(100) surface. In a 2:1 metal:ligand ratio, only half of the platinum is oxidized to the +2 oxidation state, with the remainder coordinating to the ligand without charge transfer, as Pt$^0$. The resultant Pt$^0$/Pt$^{II}$ mixed valence structure is thought to form due to the aversion of the ligand towards a four-electron reduction and the strong preference of Pt towards 0 and +2 oxidation states. Scanning tunneling microscopy reveals irregular chain structures that are attributed to the mixture of Pt valence states, each with distinct local coordination geometries. Tetraethyltetra-aza-anthraquinone (EtTAAQ), utilizes a quinone backbone with adjacent pyrazine rings to generate four symmetric binding pockets. EtTAAQ has the capacity for up to a four-electron reduction, enabling the possibility for bimetallic sites between ligands. Surface studies conducted on the Au(111) surface demonstrate TAAQ complexation with Fe at different stoichiometric ratios of Fe:TAAQ as Fe 2p core level shifts. The formation of a surface structure seen in STM images also provides evidence that metal-ligand complexation has occurred, even though multiple binding motifs are present, which produce meandering chain structures. These studies advance our understanding of metal-organic complexation in surface environments toward greater complexity and chemical functionality.

**COLL 328**

**Chemical self-assembly strategies for designing molecular electronic circuits**

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A self-assembly process in which extended oligomeric structures grow parallel to a surface is described based on isocyanide-containing molecules, in particular, with 1,4-phenylene diisocyanide (PDI), which forms long, one-dimensional chains when adsorbed on a Au(111) surface. It is found that the isocyanide functionality binds strongly enough to gold to extract gold atoms from low-coordination sites on a Au(111) surface to form one-dimensional Au-PDI structures that incorporate gold adatoms such that the π-conjugation is maintained throughout the oligomeric species. The self-assembly pathway is explored using density functional theory calculations, imaging and spectroscopy. It is also found that the oligomers are capable of bridging between gold nanoparticles on a mica or silica substrate thereby providing a conductive link between them. In this case, PDI oligomerization is self-limiting since the edge sites on the gold nanoparticles act as both nucleation and propagation sites. This provide a strategy for specifically forming conductive linkages between nanoparticles by adjusting the spacing between them.

**COLL 329**
Balancing noncovalent interactions in self-assembly of nonplanar aromatic carboxylic acid linkers at the solution/solid interface: Progress toward 2D SURFMOFs synthesis

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This study explores directed noncovalent bonding in the self-assembly of nonplanar aromatic carboxylic acids on metal surfaces for the purpose of developing design strategies to create 2D surface metal organic frameworks (SURFMOFs). The acid linkers used are ethene based and are typically employed in the synthesis of 3D MOF crystalline solids. The two-dimensional structures formed from these molecules on HOPG and Au(111) are studied by scanning tunneling microscopy (STM) in solution environment. The process of the monolayer formation and final surface linker structures are found to be strongly dependent on the combination of molecule and substrate used and are discussed in terms of intermolecular and molecule-substrate interactions, bonding geometry and symmetry of the acid molecules. In the case of the linker self-assembly on HOPG, the molecule-substrate interactions play a decisive role in the resulting surface structure. When the acid molecules are adsorbed on Au(111), the intermolecular interactions tend to dominate over the weaker molecule-substrate bonding. Additionally, the interplay of the π-π interactions and hydrogen bonding that direct the surface self-assembly on the different supports can be controlled by varying the linker solution concentration. This is particularly applicable for the case of the acid molecules adsorbing on the Au(111) substrate. The precise control over predesigned surface structures and orientation of the nonplanar aromatic carboxylic linkers opens up an exciting prospect for manipulating the direction of SURFMOF growth in 2 dimensions and potentially in 3D. Evidence of 2D SURFMOFs formation is demonstrated by STM imaging of the initial stages of coordination reactions between transition metal (+2) ions and preassembled carboxylic acid linker monolayers at the solution/solid interface.

COLL 330

Conformal surface-anchored metal-organic frameworks: Characterization of thin film growth, porosity, and electronic transport

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Toward the integration of metal-organic frameworks (MOFs) for energy storage applications, the thin film formation of two copper-paddlewheel MOF systems (MOF-14 and MOF-399) was investigated. Surface-anchored MOFs (SurMOFs) were fabricated by the sequential, alternating, solution-phase deposition of the inorganic and organic ligand precursors that result in conformal films via a van der Merwe growth mechanism.
This is in contrast to most surMOF films that follow a Volmer-Weber growth mechanism with isolated crystallites that nucleate and ripen. For the surMOF systems within our study, atomic force microscopy imaged a smooth film morphology with surface roughness determined by the underlying substrate. By developing an etch process to selectively remove the film, the physical thickness of the film was characterized by AFM revealing linear film growth as a function of deposition cycles permitting nanometer-resolution control of film thicknesses ranging from 5 to 50 nm. Electrochemical impedance spectroscopy was used to evaluate the electronic transport properties of the MOF systems. The inherent porosities of the SurMOF films were confirmed by cyclic voltammetry redox probe characterization using ferrocene. The layer-by-layer deposition of these SurMOF systems provides a promising route to incorporate MOFs as thin films with nanoscale thickness control and low surface roughness for electrochemical devices.

**COLL 331**

**H-bonded and metal-organic coordination networks on graphene**

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Molecular self-assembly on graphene has attracted increasing attention over the past few years due to its potential for applications ranging from organic electronics over photovoltaics to spintronics. On the one hand, the chemical inertness and the low density of states near the Fermi level make graphene a perfect choice as a buffer layer to decouple adsorbed molecules from the underlying (metallic) substrate. Importantly, this holds the promise to preserve the intrinsic properties of the adsorbed species such as magnetic or catalytic properties. On the other hand, molecular self-assembly on graphene can be also employed as a promising method for tuning the electronic properties of graphene (doping or band gap opening) on a macroscopic scale while for this purpose, the molecule graphene interaction has to be larger than a mere physisorptive one.

In my presentation I will discuss the structural and electronic properties for two molecule-graphene systems. For the first system, 1,3,5-benzenetribenzoic acid on graphene/Cu(111), different coverage dependent assemblies were observed. [1] We could demonstrate that the underlying Cu(111) surface influences the structural arrangement of the molecules. With respect to the electronic properties, angle-resolved photoemission spectroscopy measurements showed n-doping of graphene. For the second system, parahexaphenyl-dicarbonitrile (NC-Ph₆-CN) on graphene, we observed the arrangement of a close-packed structure independent of coverage. However, a non-negligible influence of graphene on this arrangement with a peculiar shift of every 4th molecule was detected, which was not observed for the case of metallic substrates or for the bulk phase. Adding Cu adatoms to submonolayer coverage of NC-Ph₆-CN resulted in the formation of metal-organic coordination networks with varying arrangements in dependence of the stoichiometry between molecules and Cu atoms.
With scanning tunneling spectroscopy we characterized the electronic properties and could identify differences between the different assembly structures. [2]

**COLL 332**

**Role and tracking of weak interactions in adsorbed layers on surfaces**

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In molecular systems where the molecule-surface interactions are weak, the resulting molecular assemblies usually show a well-defined range order that is driven by the intermolecular interactions and the molecule-substrate structure matching. The presence of metal adatoms on surfaces induces additional structural constrains and creates anchoring sites on which molecules become strongly bonded. In most cases, the presence of such metal adatoms within an ordered molecular network cannot be clearly revealed by imaging techniques such as STM microscopy. With the help of DFT and STM simulations, we have investigated the formation of organized adlayers in the absence and presence of metal adatoms. Although DFT calculations allow to accurately explore the configurational space of molecular adsorption, STM contrasts can be used to reveal signatures of weak interactions. In this presentation, I will show a few examples where such STM signatures are used to discriminate between adsorption sites where subtle molecule-surface interactions can be probed with STM. In addition, a new developed STM simulation package to investigate large scale molecular systems will be introduced.

**COLL 333**

**Organic, 2D transition metal dichalcogenide interface**

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We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure and local electronic properties of 2D MoS$_2$ and WSe$_2$ monolayers on HOPG substrates, and show that the electronic bandgaps can be tuned by strain at grain boundaries and dislocations [1,2]. Using PTCDA as a prototype semiconductor organic molecule, we show that a monolayer transition metal dichalcogenide (TMD) can effectively screen an organic-inorganic heterointerface [3]. We demonstrate the fabrication and unravel the electronic properties of a lateral doped/intrinsic heterojunction in 2D WSe$_2$, partially covered with a molecular acceptor C$_6$F$_{48}$ [4]. We also demonstrate the self-assembly of DAP molecules into a hexagonal porous network on a monolayer MoSe$_2$ surface, as a result of the different electron affinities of the inversion domain boundaries and the pristine MoSe$_2$ domains [5].

**COLL 334**
Topology and electronic coupling in the assembly of nanoparticle superlattices

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Colloidal nanocrystals offer a route toward engineering new classes of materials by acting as discrete units that can be assembled to construct composite solids. The self-assembly of two sizes of spherical nanocrystals has revealed a surprisingly diverse library of structures. To date, at least fifteen distinct binary nanocrystal superlattice (BNSL) structures have been documented. The stability of the observed binary phases cannot be fully explained using the traditional conceptual framework treating the assembly process as entropy-driven crystallization of rigid spherical particles. We evaluate new theoretical models treating the co-crystallization of deformable spheres and to formulate new hypotheses about the factors affecting the nucleation and growth of the binary superlattices. The deviation from hard sphere behavior can be explained by specific topological textures developed within deformable layers of surface ligands. Our results also suggest that the relative abundance of BNSL phases is determined not only by their thermodynamic phase stability but also by a postulated pre-ordering of the binary fluid into local structures with icosahedral or polytetrahedral structures prior to nucleation.

Strong electronic coupling between individual nanocrystals within a superlattice is an important prerequisite for the emergence of non-additive physical properties. However, a simultaneous realization of strong electronic coupling and dense ordered packing of nanocrystal solids has remained elusive. We report a method for growing all-inorganic highly ordered solids of nanocrystals with the interstitial space filled with a glassy metal chalcogenide matrix which, combined with the short separation between particles leads to very strong electronic coupling. Temperature-dependent conductivity measurements show metallic transport across our supercrystals. The formation of strongly-coupled all-inorganic nanocrystal assemblies represents an important step toward the bottom-up design of functional nanostructured composites.

COLL 335

Synthesis of morphology controlled Zn-chalcogenide nanocrystals: A few surprises

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Semiconductor nanocrystals (NCs) exhibit excellent optical and electronic properties, tunable by their size and shape dependent quantum confinement effect. However, the successful materials with incredible achievements mostly contain heavy metal elements. Unfortunately, the toxicity and related regulatory aspects impede further wide spread implementation of these colloidal semiconductor NCs. Considering this, and the high interest in furthering the accomplishments of colloidal chemical control demonstrated for the Cd-chalcogenides, it is an important challenge to explore and
develop new heavy-metal free semiconductor NCs. In particular, we consider a seemingly minor change from cadmium- to zinc-chalcogenides, which naively would appear as an easy translation of the chemical synthesis principles to a closely related element system. We will present various approaches for the synthesis of Zn-chalcogenide nanocrystals, in particular with regards to shape control of these systems. A few surprises are revealed, including the formation of nanorod couples as one example. Moreover, hetersotructures including Zn-chalcogenides dumbbells will be described. Controlling the shell morphologies from flat to islands to a unique helical shell architecture will be presented. Aspects pertaining to the structure-function relationships for these architectures will also be discussed.

COLL 336

Surface chemistry of lead halide perovskites nanocrystals

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Following a surge of interest in lead halide perovskites, research on colloidal nanocrystals of these materials has gathered momentum in the last years. In such a narrow time span, several properties/features of halide perovskite nanocrystals have been investigated, among them electroluminescence, lasing, anion-exchange, as well as control of size and shape such that nanocrystals in the quantum confinement regime can now be easily fabricated, with narrow size distributions. One aspect that remains less explored is the surface chemistry of these nanocrystals. Ligand binding in this case is very dynamic and can be strongly influenced by the external environment. The present talk will highlight the research activities of our group on understanding surface ligand binding and how this influences the synthesis, stability, optical properties, and post-synthesis transformations of colloidal lead halide perovskite nanocrystals.

COLL 337

Synthesis and assembly of chiral nanoparticles

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Chiral nanostructures represent one of the fastest growing fields of nanoscience and technology with broad impact from biology to information technologies. Multiple studies indicate that one can synthesize a large library of chiral nanoparticles (NPs) with controlled handedness. Their self-organization results in chiral superstructures at larger scales and illustrates the importance of subtle anisotropic effects stemming from collective behavior of NPs and non-additivity of their interactions. Distinct similarities between the geometries and light-matter interactions involving chiral supramolecular and biological systems can also be traced. They can be seen in the synthesis and
separation methods, chemical properties of individual NPs, geometries of the
nanoparticle assemblies, and interactions with biological counterparts. The analysis of
these similarities with known biological, supramolecular, and liquid crystalline materials
help us understand in greater depth the role of chiral asymmetry in Nature and
accelerate the development of technologies based on chiroplasmonic, chiroexcitonic,
and chiromagnetic effects. Technological prospects of chiral inorganic materials with
current front-runners being biosensing, chiral catalysis, polarization optics and chiral
photonics will be discussed in this talk.

COLL 338

Making nanoscale chemistry matter: Synthesis & assembly

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Materials science and chemistry are intimately linked, particularly at the nanoscale,
where chemical interactions drive the assembly process. Precise control of chemistry
enables the emergence of a “material”, critical for the bottom-up assembly of colloidal
nanoparticles, surfaces, and related systems. Here we discuss emerging assembly
techniques from the perspective of materials application, showcasing recent innovations
at the chemistry/material interface. Ultimately, the produced structural and functional
building blocks have application for many technologically significant materials and
devices. As such, we also outline a method to assess research progress in published
works, to contextualize the stage of material development in terms of broader societal
impact - i.e., making nanoscale chemistry matter.

COLL 339

Colloidal cesium and formamidinium lead halide perovskite nanocrystals:
Genesis, properties and applications

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We discuss the discovery, recent developments and prospects of colloidal lead halide
perovskite nanocrystals (LHP NCs, NCs, A=Cs+, FA+, FA=formamidinium; X=Cl, Br, I)
[1,2,3,4,5]. LHP NCs exhibit spectrally narrow (<100 meV, 12-45 nm from blue-to-near-infrared)
sponaneous and stimulated emission, originating form bright triplet excitons [6], and
tunable over the entire visible spectral region of 400-800 nm [1-4]. Post-synthetic
chemical transformations of colloidal NCs, such as ion-exchange reactions, provide an
avenue to compositional fine tuning [7]. Cs- and FA-based perovskite NCs are highly
promising for backlighting of LCD displays, for light-emitting diodes and as
precursors/inks for perovskite solar cells. In particular, high purity colloids are ideal for
further engineering as needed for photochemical/photocatalytic applications. Towards these applications, a unique feature is that perovskite NCs appear to be trap-free without any electronic surface passivation [8]. The processing and optoelectronic applications of perovskite NCs are, however, hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface capping molecules during isolation and purification. To address this issue, we have developed a new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules [9]. Perovskite NCs also readily form long-range ordered superlattices. These assemblies exhibit accelerated coherent emission (superfluorescence) [10].

Colloidal Lead Halide Perovskite Nanocrystals

**COLL 340**

**Strong plasmon-exciton coupling in colloidally assembled Au quantum-dot structures**

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Light-exciton interaction can be highly modified when excitons strongly couples to a plasmonic nanocavity, giving rise to a hybrid plasmon-exciton state. In this regime the energy exchange rate between the plasmon and exciton exceeds any other decay process and lead to the splitting in both the dark-field scattering and fluorescence
spectra of the structure. Here we used colloidal assembly method to fabricate sanwiched Au-quantum dot-Au structures to demonstrate the impact of mode volume of the plasmonic cavity on the coupling strength. We carefully selected the quantum dot and the gold nanoparticles so that the fluorescence of the exciton aligns with transverse mode of the gold nanoparticle dimer. With decreased gap size of the gold dimer, we observed the splitting effect of both dark-filed scattering and fluorescence spectra from individual hybrid structures. Transmission electron microscopy was applied to obtain the morphology of the structures that correlates with their optical spectra further. The correlated study confirms the origin of the peak splitting is due to the strong plasmon-exciton coupling.

COLL 341

Simple class of responsive liposomes that transform into micelles upon heating

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Liposomes (vesicles) are spherical nanocontainers formed by the self-assembly of phospholipids in water. They are widely used as nanocarriers for drug-delivery. Payloads encapsulated in the aqueous core of liposomes can be released slowly by passive diffusion through the lipid bilayer. Alternately, the payload can be released en masse if the liposomes are converted into micelles (note that micelles, unlike liposomes, have a hydrophobic core). Recently, there has been much interest in devising liposomes that can be induced to transform into micelles by external stimuli such as temperature, pH, or light. Such responsive systems have been investigated in the context of formulations for drug-delivery. Many of these responsive liposomes are based on specially synthesized lipids or on mixtures of lipids with single-tailed surfactants.

Here, we demonstrate that a thermally induced transition of liposomes into micelles can be realized in a very simple system that uses only a single phospholipid. We work with soy lecithin, a lipid with a phosphatidyl choline headgroup that is inexpensive and commercially available. The responsive system is obtained by forming liposomes of the lecithin in mixtures of water and a co-solvent such as ethanol. Liposomal samples at low ethanol fractions remain unchanged as a function of temperature. However, when the ethanol fraction crosses a threshold value, the samples undergo a transition from a turbid dispersion of liposomes (~ 100 nm diameter) at room temperature to a clear solution of spherical micelles (~ 5 nm diameter) above a critical temperature. The critical temperature can be varied by changing the water:ethanol ratio. Small-angle neutron scattering (SANS) and cryo-electron microscopy (cryo-EM) are used to confirm the above microstructural transition. To understand the fundamental origins of the above transition, we have investigated the temperature-dependent phase-behavior of lecithin/water/alcohol mixtures over a wide range of compositions. The discovery of
thermal transitions in these simple liposomal systems could prove useful in both medical and cosmetic formulations.

**COLL 342**

**Annexins induce membrane curvature near hole edges during plasma membrane repair**

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Maintaining integrity of the plasma membrane is essential for cell life. Thus, efficient cell membrane repair mechanisms are crucial for handling membrane disruptions resulting from external perturbations of eukaryotic cells. Cancer cells experience enhanced membrane stress when navigating through the dense extracellular matrix, which increases the frequency of membrane injuries. Yet the underlying molecular details of plasma membrane repair are not well understood.

Plasma membrane injury followed by Ca\(^{2+}\) influx, activates the recruitment of Annexins to membrane wound edges. In cancer cells subjected to localized laser damage, we find that binding of several annexin members promotes the repair of lesions. In a planar model membrane system consisting of round membrane patches, we show that curvature stress induced by Annexin A4 leads to roll-up of the membrane as initiated from free membrane edges. The rolling process is deduced by analysis of time-lapse fluorescence images, combined with AFM on the same sample region. We have characterized the effect of 9 human annexins on membranes and shown that they induce distinct morphologies which can all be attributed to curvature.

The observation of rolling identifies membrane curvature near hole-edges as a potential key event in the plasma membrane repair (PMR) process. In the geometry of a membrane hole we propose that spontaneous curvature coupled with line tension leads to the formation of a characteristic neck structure around the hole as the first step in the repair process. Formation of a neck geometry is further supported by theoretical modeling.
Annexin-induced rolling of a double supported membrane patch measured by time-lapse fluorescence.

**COLL 343**

**Molecular interactions between cell membranes and surface immobilized peptides**

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Surface immobilized antimicrobial peptides are extensively used for antimicrobial coatings, bacteria capture, and bacteria sensing. It was shown in the literature that free peptides in solution can penetrate into bacterial cell membrane to disrupt cell membrane to kill bacteria. However, the interaction mechanisms between the bacteria cell membranes and surface immobilized peptides are not fully understood. We have applied a nonlinear optical spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, to investigate molecular interactions between surface immobilized
peptides and model bacterial cell membranes as well as live bacteria in situ at the molecular level. It was found that the peptides do not penetrate into cell membranes, instead, they tilt more towards the surface. We believe that surface immobilized peptides kill bacteria because of the charge interaction, instead of membrane insertion. A fluorescence microscope was constructed which can be used to image the same sample while SFG spectra are collected, measuring structure and function at the same time during the peptide-membrane interaction.

**COLL 344**

**Lipid self-assembly in bulk and at interfaces: Non-lamellar phases and biomolecular interactions**

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Non-lamellar lipid aqueous phases, such as reverse cubic or hexagonal phases, can be used to entrap smaller biomolecules. The curvature of these lipid phases and hence the size of the aqueous cavities depends on the composition, water content and temperature. The challenge is to encapsulate proteins, such as large enzymes due to the limited size of these cavities. Here, we will present a lipid system, based on mixtures of acylglycerides and acyldiglycerides, which are able to form highly swollen sponge phases (L₃), with aqueous pores up to 13 nm of diameter. The structure and composition of the particles were revealed by using small angle neutron scattering (SANS), light scattering, cryo-TEM, size exclusion chromatography and Raman spectroscopy. The results for the sponge phases are compared with data for lamellar and reverse bicontinuous cubic phase in the same lipid system. Large similarities in lipid chain confirmation and head group interactions are observed as all three structures are formed by lipid bilayers, albeit of different curvature. The L₃ structure in excess aqueous solution form sponge-like nanoparticles (L₃ NPs). We investigate encapsulation of two key types of enzymes of different sizes, used in food processing, namely Aspartic protease (34 KDa) and Beta-galactosidase (460 KDa). They are today delivered into the process as solutions with a considerable amount of preservatives and still with limited shelf-life and limited control of the enzyme activity. The SANS results reveal differences in the L₃ NPs with and without enzyme that can be interpreted as inclusion of the protein in the liquid crystalline phase. These findings are verified by size exclusion chromatography and the enzymatic activity of the encapsulated enzyme, which surpasses the storage stability of pure enzymes in solution. To reveal the nature of the
interaction between the enzymes and the lipid matrix, we further studied the adsorption of both proteins on the lipid layers formed by the L₃ NPs. These data reveal partial penetration of the enzymes in the lipid bilayers. The lipid self-assembly structure can also be changed in desired way by adding a particular type of lipolytic enzymes. Here the (oil) triglyceride aqueous interface is important also for other processes like emulsification. Our results using ellipsometry and x-ray scattering show that uptake of water in the triolein phase can occur and this can be affected by the presence of lipolytic enzymes.

COLL 345

Mapping membrane receptor dynamics, self-association, and oligomerization: Applications of homo-FRET and super-resolution microscopy

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Membrane receptor interactions and dynamics are intimately coupled with their local environment and often self-association state. We have been exploring the oligomerization behaviour and dynamics of the CEACAM family of membrane receptors. By coupling homo-FRET microscopy, as our primary approach for characterizing monomer-dimer-oligomer in live cells, with super-resolution techniques such as STORM, we are now able to explore the oligomerization - spatial localization landscape for CEACAM and its implications for inter-cellular activation and signalling.

COLL 346

Direct comparison between molecular lateral diffusion constant and lipid membrane viscosity using quasi-elastic neutron scattering techniques

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Lipid membranes are highly dynamic to accommodate the motions of biological molecules and bilayer deformations needed in cell functions. Yet compared to our understanding of the structural integrity of complex biomembranes, much less is known about the membrane dynamics. Neutron scattering techniques are uniquely suited to provide important insights into structure and dynamics of lipid membranes as they access materials properties in atomic to molecular length and time scales. Some of us have developed a probe-free means to estimate the membrane viscosity through measurements of the collective thermal fluctuations of lipid bilayers using neutron spin echo (NSE) spectroscopy. The membrane viscosity is one of two key parameters that
characterizes the membrane transport properties, the other is the molecular diffusion constant of molecules within the membrane. According to a theory proposed by Saffman and Delbrück for two-dimensional molecular diffusion in a membrane, the molecular diffusion constant is non-linear in both the size of the molecule and the membrane viscosity. Studies of protein, particles, and lipid domains of different sizes in membranes have confirmed the non-linear dependence of the diffusion constant on the molecular size. However, no direct comparison between the molecular diffusion constant and membrane viscosity has been reported. Here, we combine neutron backscattering measurements of the lipid diffusion constant (\(D\)) and NSE measurements of the membrane viscosity (\(\eta_m\)) and show that \(D\) is linearly proportional to \(\eta_m^{-1}\). Together these results show that the predicted nonlinearity for \(D\) on \(\eta_m\) is not significant for common saturated lipid bilayers in water.

**COLL 347**

**Understanding the mechanism of antimicrobial peptides using small-angle x-ray and neutron scattering techniques: The lipid’s point of view**

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It is generally believed that antimicrobial peptides, AMPs, are able to evade much of the bacterial resistance because they disturb the fundamental integrity of the entire cell by interfering with the life-defining cell membrane. However, there is no clear general consensus for the molecular basis by which AMPs act, although various structural modifications such as membrane deformation or pore formation have been suggested. [1,2] However, other factors may contribute such as changes in the lipid dynamics, changes in the lateral and transversal lipid composition and enhanced proton/ion transfer.

In order to fully understand the mechanism, we embarked on a study to investigate both the structural and dynamic effects on model membranes. To this end we employed state-of-the-art Small-angle X-ray and neutron scattering (SAXS/SANS) methods which are capable to probe the structure of both lipids and peptide on nanometer length scales. In addition, by using H/D contrast variation scheme we could determine the lipid dynamics extracting both the transversal flip flop motion as well as lipid exchange. We will show using indolicidin as a model AMP, that the peptide significantly alters the lipid dynamics without significantly altering the structure of the bilayer. The results further show that indolicidin inserts on the interface between lipid tail/head on the outer leaflet perturbing the lipid packing causing an acceleration in the dynamics. We speculate that the change in dynamics among others, leads to enhanced ion transport that is detrimental to the bacterial cell.

**COLL 348**

**Heterogeneous dielectric implicit membrane model for the calculation of MMPBSA binding free energies**
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Membrane-bound protein receptors are a primary biological drug target, but the computational analysis of membrane proteins has been limited. In order to improve Molecular Mechanics Poisson-Boltzmann Surface Area (MMPBSA) binding free energy calculations for membrane protein-ligand systems, we have implemented a new heterogeneous dielectric implicit membrane model into the Amber software suite. This new model supersedes our previous uniform, single dielectric implicit membrane model by allowing the dielectric constant to vary with depth within the membrane. We calculated MMPBSA binding free energies for the Human Purinergic Platelet Receptor (P2Y₁₂R) bound to various agonist and antagonist ligands using both models, and we found that the new model has a stronger correlation with experimental binding affinities compared to the older model. This improved membrane model increases the utility of MMPBSA calculations for the rational design and improvement of future drug candidates.

COLL 349

Growing supergiant liposomes on nanocellulose paper and regenerated cellulose membranes

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Giant unilamellar vesicles (GUVs) are useful in vitro models for biophysical experiments. We had recently reported that cellulose paper and fabric promotes the vesiculation of lamellar phospholipid stacks to form GUVs. The cellulose-abetted method rapidly produced GUVs with a variety of lipid types in a simple power-free format. Despite these advantages, quantitative analysis showed that GUV sizes were typically limited to below 20 micrometers. For some applications in synthetic biology, GUVs with sizes larger than 50 micrometers are desirable. Here we demonstrate that smooth nanocellulose and regenerated cellulose substrates produces GUVs from lamellar phospholipid stacks. GUVs of larger diameters were obtained on the nanostructured surfaces due to the increased merging of the GUV buds on the surface. Super giant vesicles with diameters > 100 micrometers were regularly obtained. The use of nanostructured surfaces increased yields of GUVs compared to cellulose paper and fabric. The yield of GUVs from the nanostructured surfaces was higher than the yield of GUVs obtained through electroformation. Thus, this method shows promise as a means for the sustainable fabrication of GUVs at the laboratory scale and larger.

COLL 350

Self-assembly of nanoparticles into two-dimensional arrays for catalytic applications
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Self-assembly of nanoparticles (NPs) is at the heart of nanotechnology, and has shown many potential applications in fabricating nanodevices with highly controlled functionality. Two-dimensional (2D) arrays of NPs can provide a thin and uniform NP array with each NP being exposed on the surface to maximize NP catalysis. This talk summarizes our recent efforts on the fabrication and application of 2D NP arrays for oxygen reduction reaction, oxygen evolution reaction, selective CO\textsubscript{2} reduction, and efficient one-pot reaction to functional molecules. The talk intends to demonstrate that creation of libraries of NP arrays with varying chemical/catalytic properties is an exciting direction in catalysis, and may be used to solve complicated catalytic problems in which multiple chemical reactions need to be catalyzed in a single reaction vessel.

**COLL 351**

**Use of ligand-binding to form low-index facet metal nanocrystals for catalysis**

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Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The use of ligand binding is an important strategy to control the growth and final shape of nanocrystals and will be discussed. The results presented will include the formation of catalytic metals such faceted and branched nanostructures containing gold, palladium and ruthenium. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Catalytic applications will be discussed with a focus on branched ruthenium based systems for electrocatalysis of the oxygen evolution reaction shown below.
Figure: a) Low resolution TEM image of Pd-Ru core-branched nanoparticles. b) High resolution TEM images (left) and corresponding models (right) showing the positions of hcp-Ru branches around fcc-Pd cores of monopod and bent bipod nanocrystals.

COLL 352

Tailoring surface structures of spongy metallic nanoparticles toward optimization of electrocatalysis

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Spongy metallic nanoparticles adopting a 3D solid/void bicontinuous architecture exhibit a unique set of structural features, such as large surface-to-volume ratios, easily accessible 3D open surface structures, high density of surface active sites, conductive skeletal frameworks, tailorable local surface atomic coordination, and tunable surface compositions, all of which are highly desired for optimization of electrocatalysis. However, it still remains challenging to fully unravel the detailed structure-composition-property relationships underpinning the electrocatalytic behaviors of the spongy metallic nanoelectrocatalysts due to the intrinsic structural complexity of the materials systems and the synthetic challenges associated with precise control over the atomic-level surface structures of the nanoparticles. Here I will talk about two wet chemistry approaches we recently developed through which multimetallic alloy nanoparticles controllably transform into spongy metallic nanoparticles with fine-tailored surface atomic coordinations and surface compositional stoichiometries. The first approach involves the nanoporosity-evolving percolation dealloying of alloy nanoparticles under kinetically controlled conditions and the second approach is based on judicious manipulation of the interplay among galvanic exchange, oxidative etching, and seeded deposition. Success in structure-controlled nanoparticle synthesis further allow us to
correlate the activity, durability, and selectivity of the spongy metallic nanoelectrocatalysts with their detailed structural and compositional characteristics using hydrogen evolution reaction and oxidation of liquid alcohols and glucose as model electrocatalytic reactions. The insights gained from this work provide key design principles guiding the rational architectural tailoring of metallic nanoelectrocatalysts toward performance optimization for a variety of important electrochemical reactions.

COLL 353

Surface-driven magnetism of Fe-oxide nanocrystals

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In ferrimagnetic oxide nanoparticles surface structural disorder may lead to spin disorder (see figure, left panel), which will impact on the magnetic properties of particles with such large surface/volume ratio. In this presentation I will show how to detect the presence of such surface (spin) disorder using simple magnetometry techniques, namely the well-known field-cooled hysteresis loops (an example is shown in the Figure) and the recently reinterpreted remanence plots (delta M and Henkel). Data will be shown for several batches of highly uniform maghemite nanocrystals in the diameter range 6-11 nm, which have been isolated by thick silica shells grown by microemulsion (see Figure) to prevent interactions effects. The results are correlated to high-field Mössbauer spectroscopy and X-ray diffraction.
**COLL 354**

**Carbon nitride compounds for heterogeneous photocatalysis**

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The environmental treatment and clean energy production represents one of the hardest challenge in the next future and the photo-catalysis represent a reliable promising solution. A further step with respect the well-known inorganic semiconductors already utilized, like titanium dioxide and zinc oxide, is represented by organic/inorganic photocatalytic materials: cheaper, more versatile in chemical and in the flexible designs. Among the others, Carbon nitride compounds are recently increased their importance for energy and sustainability applications ranging from visible-UV light harvesting and photo-catalysis, to fuel cell and catalyst supports.

In this talk we will go deeper in the surface interaction among Carbon nitride and Titanium dioxide.

The fundamental role of the surface termination will be shown also by the possibility to tune the crystal structure of TiO$_2$ nanocrystal by using low intensity monochromatic lights.

Specific ALD growth of hybrid samples on two different inorganic layers, alumina and titania, are discussed to outline the effects of the precursor and gas reactivity on Carbon Nitride compounds with different surface terminations.

Finally, we present a new hybrid system by using an ordered mesoporous TiO$_2$ structure and a new phenyl modified g-C$_3$N$_4$ compound. The strong interaction between organic compound and the surface of metal oxide nanocrystals has been utilized to enhance the catalytic performance of a new heterogeneous catalyst. The promising photocatalytic behavior will be shown and X-Ray diffraction, UV, time resolved and steady time photoluminescence, infrared and Raman spectroscopy measurements will be presented and discussed.

**COLL 355**

**Surface-modified magnetic nanoparticles as efficient adsorbents for heavy metal removal from wastewater: Progress and prospects**

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The great amount of research on magnetic nanoparticles for application in wastewater decontamination has generated new and exciting materials in recent times. The effect of magnetic nanoparticles must be known to show low cytotoxicity and be ascertained prior to their use for wastewater treatment. Synthesized chelating ligands considerably improve the adsorbing capabilities of magnetic nanoparticles in wastewater. This paper (with over 100 refs) discusses the influence of surface modification on the efficiency of
magnetic nanoparticles for the removal of heavy metals in wastewater. The progress made on or/and prospect of magnetic nanoparticles functionalization for wastewater decontamination are also extensively highlighted. This review is specifically targeted at reviewing the different strategies that could be employed for surface modification of magnetic nanoparticles for application in the removal of heavy metals from wastewater.

**COLL 356**

**Rearrangement of bimetallic alloys: understanding through surface science models**

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Silver/Palladium alloys are used in heterogeneous catalysis as a means of improving reaction selectivity. Palladium deposited on Ag (1 1 1) is used as a model to understand rearrangement of the material in the presence of reactive gases. Thermodynamically, Pd is a more stable in the subsurface region; leading to silver-capped palladium islands after heating to 450 K. The Palladium migrates to the surface upon exposure to CO or O₂ at room temperature. A combination of ambient pressure X-Ray photoelectron spectroscopy, scanning tunneling microscopy, and density functional theory were used to understand the dynamic behavior of these materials. Selected examples of reactivity that illustrate the bifunctionality of the material will be presented.

**COLL 357**

**Control of charge transfer into large organic molecules on ultrathin MgO(001) films**

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Charge transfer processes on ultrathin, supported oxide films have received increasing attention in recent years because of the possibility to control the charge state of adsorbates or the direction of catalytic reactions. The main driving forces for the occurrence of charge transfer in these systems is the reduction of the substrate work function induced by deposition of the oxide film in combination with an adsorbate with high electron affinity. While previous studies have focused on the charging of metal atoms (e.g. Au) or small molecules (e.g. O₂, NO₂), we have recently extended these investigations into charge transfer processes to large organic molecules. In this
contribution, we present results on the adsorption and charging of pentacene (5A) and
tetraphenylporphyrin (2H-TPP) on ultrathin MgO(001) films supported on Ag(001). By
combing scanning tunneling microscopy and photoemission spectroscopy and
tomography, we are able to identify and quantify charge transfer into the organic
monolayer film. In addition, we show that by variation of the work function and the MgO
thickness it is possible to drive the system into a state where no charge transfer occurs.
In the case of 2H-TPP charge transfer also appears to strongly influence the self
metalation of 2H-TPP to Mg-TPP. Thus, our investigations lay the basis for the ultimate
control of charge transfer, and the related chemistry, on ultrathin oxide film systems.

COLL 358

Highly active FeNi bimetallic phosphide catalyst gives unprecedented selectivity
to the direct desulfurization pathway

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Hydrodesulfurization (HDS) of petroleum feedstocks is an area of great importance in
the refining industry because the sulfur content of available crude feedstocks is steadily
increasing, while at the same time the oil is becoming heavier. Transition metal
phosphides have attracted attention as new catalysts for hydrodesulfurization with
activity higher than conventional sulfides. Early work showed that the activity of
common phosphides follows the order: Ni2P > WP > MoP > CoP > Fe2P and the high
activity of Ni2P is the subject of this presentation. A study of Ni and Fe phosphide alloys
allows identification of the active site.
The bulk structure of Ni2P consists of tetrahedral Ni(1) sites and square pyramidal Ni(2)
sites in Ni2P and the role of the sites was studied by substitution of Ni with Fe. The Fe
component was deemed as a good probe because Ni2P and Fe2P adopt the same
hexagonal crystal structure, yet Fe2P is completely inactive for HDS. For this purpose a
series of NiFeP/SiO2 catalysts were prepared with different Ni:Fe molar ratios (1:0, 3:1,
1:1, 1:3, and 0:1) and investigated in the HDS of 4,6-dimethyldibenzothiophene (4,6-
DMDBT) at 300 and 340 °C. The uniformity of the NiFe series was demonstrated by x-
ray diffraction analysis and by Fourier transform infrared (FTIR) spectroscopy of
adsorbed CO. The position of substitution of Fe was determined by extended X-ray
absorption fine structure (EXAFS) analysis. It was found that at 300 °C the HDS activity
of the catalysts decreased with increasing Fe content and that this could be explained
by the substitution of Fe at the more active Ni(2) sites. As temperature was raised to
340 °C, the activity of the Fe-containing samples increased dramatically almost to the
level of Ni2P, and this could be understood from a reconstruction of the NiFe phase to
expose more Ni(2) sites. This was likely driven by the formation of surface Ni-S bonds,
which could be observed by EXAFS in spent samples. The extremely high activity of the
NiFe catalyst was accompanied with an unprecedented increase in the selectivity of HDS toward the direct desulfurization pathway, with the major product being dimethylbiphenyl.

**COLL 359**

**Ionic liquid adsorption and ion exchange processes at single crystal surfaces**

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Thin films of ionic liquids (ILs) have been in the focus of ultra-high vacuum (UHV) surface science in the past ten years as they provide a powerful route for molecular level studies of liquid/solid interfaces in general. The detailed knowledge of the structure and the formation of the IL/solid interface enables a more complete description and control of the interface properties and the system's overall stability and performance in applications where ILs are in contact with solid surfaces, such as catalysis. In this contribution, we summarize recent results on ultrathin IL films, which have been prepared by *in situ* physical vapor deposition. We particularly concentrate on processes that occur in mixtures of two different ILs, which were successively deposited on Ag(111) as model support. By temperature-dependent angle-resolved X-ray photoelectron spectroscopy, we found pronounced surface and interface enrichment effects due to rapid ion exchange processes. We propose that the phenomena observed in these films are driven by the interplay of interface adsorption energy at the liquid solid/interface and the surface free energy at the liquid/vacuum interface.

**COLL 360**

**Selectivity in hydrogenation catalysis**

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In this presentation we will survey some of the recent advances in our research on the understanding of the factors that affect selectivity in the hydrogenation of organic molecules promoted by platinum catalysts. In the first of three themes, we elaborate on the progress made in our laboratory in our study of the role that carbonaceous surface deposits play in the hydrogenation of olefins and on the kinetics of hydrogen adsorption-desorption and diffusion under catalytic conditions. We will then briefly expand on the implications of our conclusions to more complex systems, with emphasis on the selective hydrogenation of unsaturated aldehydes. The last section will be dedicated to the discussion of enantioselective hydrogenation processes using chiral modifiers.

**COLL 361**

**Engineered nanomaterials for cancer immunotherapy**
With profound advances in immune-oncology, cancer immunotherapy is now considered the fourth pillar of cancer therapy, joining the ranks of surgery, radiotherapy, and chemotherapy. For some cancers, including advanced non-small cell lung cancer, combination immunotherapy is FDA-approved as the frontline therapy, showing promise for applying immunotherapy to a wide range of advanced cancers. However, their dose-limiting toxicities and low patient response rates remain as the major challenges to address. Here, we highlight new opportunities for combination immunotherapy based on nanomedicines that are well poised to tackle the challenges faced by the field of cancer immunotherapy. We present new biomaterial-based strategies for amplifying anti-tumor immune responses and sensitizing tumors to immunotherapies in a safe and effective manner. Briefly, we show that lipid-based nanodiscs can efficiently co-deliver antigen and immunostimulatory molecules to draining lymph nodes and elicit potent CD8+ cytotoxic T lymphocyte responses directed against tumor antigens, leading to substantially enhanced anti-tumor efficacy in multiple murine tumor models, including colon carcinoma, melanoma, and HPV-induced tumors. In a second research thrust, we have shown that this nano-platform can deliver chemotherapeutic agents in a synergistic manner with immune checkpoint blockers. Owing to the facile production process, robust therapeutic efficacy, and good safety profiles, our nanotechnology offers a powerful and convenient platform for improving cancer immunotherapy.

**COLL 362**

**Glycodendron modified HES nanocapsules for targeting of dendritic cells**

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Immunotherapy has been established as a successful method for cancer treatment. The combination of immunotherapy with nanotechnology is likely to be the next step towards personalized modern medicine.

Dendritic cells (DCs) play an essential role in the induction of an antigen specific immune response. Due to their ability to modulate and initiate the immune system, DCs present one of the key targets in immunotherapy. DCs fragment foreign cell structures and upon that interact with B- and T-lymphocytes. Therefore, DCs contribute to antibody production as well as to T-cell tolerance in a preliminary manner.

The DC-SIGN receptor, that is specific for DCs and highly abundant on their cell surface, belongs to the C-type lectin superfamily. The receptor has a carbohydrate recognition domain (CRD), that consists of four binding domains. Hence, it was emphasized that binding activity of potential carbohydrate-ligands, when presented in a multivalent manner, could largely increase biological efficacy, if more than one domain is addressed.
Herein a nanocarrier-system consisting of HES (hydroxylethyl starch) nanocapsules, with covalently attached glycodendrons, as potential DC SIGN binders, on the nanocapsule’s surface is presented. These nanocarriers are prepared in an inverse miniemulsion process and are further functionalized by introduction of dibenzocyclooctyne (DBCO) groups for copper-free click chemistry. Flow cytometry and laser scanning microscopy experiments showed increased binding and receptor-mediated uptake mechanisms of these surface modified HES nanocapsules by human dendritic cells.

Receptor-mediated uptake of glycodendron-decorated HES nanocapsules by human dendritic cells by blocking of specific receptors with antibodies.

COLL 363

Local reprogramming of antigen presenting cell function using synthetic depots to promote tolerance

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During Multiple Sclerosis (MS), immune cells mistakenly attack myelin – an axon’s insulating matrix. Many of the available MS therapeutics cause susceptibility to infection. An exciting new approach is to promote antigen-specific tolerance by generating regulatory T cells. As part of the immune response, T cells are activated by dendritic cells (DCs) within lymph nodes (LN) – key immune sites. Our lab has synthesized microparticles (MPs) co-encapsulating a myelin antigen, MOG, and an
immunomodulatory molecule, rapamycin (Rapa) that are injected directly into LNs. These MPs are too large to drain from LNs, instead, slowly degrading to release MOG and Rapa. This local release permanently reverses paralysis in a mouse model of MS. We hypothesize intra-LN treatment functionally alters DCs, impacting how these cells polarize myelin-reactive T cells. To test this idea, DCs were isolated from mice treated intra-LN, then DC activation was measured by flow cytometry. These studies demonstrated DCs from MOG/Rapa MP-treated mice have an attenuated inflammatory response (Fig. 1A). Next, the impact of intra-LN treatment on DC-driven T cell proliferation was assessed by culturing DCs isolated from MP-treated mice with myelin reactive T cells. These studies reveal DCs from MOG/Rapa MP-treated mice cause reduced T cell proliferation (Fig. 1B), indicating DCs from depot treated mice exhibit altered function. Further studies will elucidate how MP treatment impacts DC trafficking and T cell phenotype. This knowledge could contribute to new antigen-specific therapies.

**Figure 1:** A) Splenic DCs were isolated from mice induced with EAE and treated intra-LN with the indicated microparticle formulation 10 days later. DCs were cultured with LPS – an inflammatory signal – for 16 hours before activation was measured using flow cytometry. There was a reduction in activation following DC stimulation with LPS – an inflammatory signal. B) DCs were obtained as in panel A and stimulated with MOG or MOG and LPS. Myelin reactive T cells were immediately added to culture and proliferation was assessed by fluorescence dilution. T cells cultured with DCs from MOG/Rapa MP treated mice displayed reduced proliferation compared to T cells cultured with DCs from Empty MP treated mice.

**COLL 364**

**Transient membrane pore-forming conjugated polymer nanoparticles**

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Conjugated polymer nanoparticles (CPNs) are formed by self-assembly of non-aqueous soluble conjugated polymers (CPs) in an aqueous solution. By introducing positive charges at the side chains of CPs, we have demonstrated non-toxic labeling of live
cells, small interfering RNA delivery, and intracellular organelle labeling. Using scanning ion conductance microscopy (SICM), we have also discovered that the hydrophobicity of CPNs plays crucial roles in inducing dramatic topographical changes in the live cell membranes, while no toxic effects were observed. In this presentation, we report transient membrane pore forming CPNs. Significant topography and extracellular surface potential changes in live human cervical carcinoma (HeLa) cells were observed after incubating CPNs for a short incubation time (i.e., ~1 h and ~4 h for guanidine- and primary amine-containing CPNs, respectively). No significant surface topographic and transmembrane potential changes were observed cells incubated at the same CPN concentration for longer incubation time (i.e., 6 h). With results from the fluorescence-based cellular entry studies, we conclude that the direct entry of CPNs through pore formation is favorable at the initial stage and conventional endocytoses become predominate when high concentrations of CPNs adsorbed on the membranes. This study provides an important observation on how the cells interact with and respond to positively charged polymeric nanomaterials, leading to developing efficient drug/gene delivery materials.

COLL 365

Designing biodegradable lipid nanoparticles for enhanced intracellular delivery and genome editing

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Lipid nanoparticles have recently been intensively studied for their potential as nanocarriers for intracellular drug delivery. The spatiotemporally controlled release of drug from nanocarriers for enhanced delivery efficiency, however, challenges an effective drug delivery. In this presentation, I will be talking that how we can use a combinatorial strategy to design and optimize the chemical structure of lipid nanoparticles to improve the delivery of protein and nucleic acid, with extended application of cancer therapy and CRISPR/Cas9 genome editing. We find that the integration of chemically degradable component into the lipids enables the efficient control of lipid degradation in live cells to release protein and nucleic acid, showing an significantly enhanced protein and RNA delivery, as well as improved genome editing efficiency. An optimized lipid nanoparticle formulation shows effective RNA interference and CRISPR/Cas9 genome editing in vivo, and is therefore of great potential to fasten the clinical translation of CRISPR/Cas9 genome editing technique.
Intracellular cytotoxic peptide release triggered by *in situ* hybridization of complementary, DNA-conjugated, multicolor carbon dots

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Triggered release of drugs has received remarkable interest from the nanotechnology community in recent years due to the obvious medical benefits this type of ‘smart’ system represents. From a complete departure from the previously attempted on-demand delivery using exogenous or intrinsically endogenous triggers, here we show that in situ hybridization can be effectively used to prompt intracellular drug release. By using complementary DNA sequences as surface ligands, we selectively allow two individual diffusing ‘dual-color’ carbon dots to interact *in situ* and *in vitro*. Spontaneous nanoscale oxidation of surface-abundant nitroso-/nitro-functionalities leads to two distinctly colored carbon dots (CD) which are isolated by polarity driven chromatographic separation. Green and red emitting carbon dots were decorated by complementary single stranded DNAs (ss-DNA) which produce a marked increase in the fluorescence emission of the respective carbon dots. Mutual colloidal interactions are achieved through hybridization of complementary DNA base pairs attached to the respective particles resulting in quenching of their photoluminescence. The observed post-hybridization quenching is presumably due to a combinative effect from a well-matched duplex DNA formation and close proximity of multi-colored CDs, having overlapped spectral regions leading to a non-radiative energy transfer process released as heat. The process of in situ hybridization can be used for triggered intracellular release of a biologically relevant molecule. An immediate application explored in this work is to use these ss-DNA conjugated complementary CDs for controlled intra-cellular delivery of cytotoxic peptides (i.e. melittin) to cells for anti-cancer therapy. Our results established the role played by the mutually-interacting complementary CDs as a
triggering mechanism to successfully release of melittin. This signifies the further exploration of such complementary CDs for controlled delivery of peptide-based DNA interacting payloads. This strategy may also contribute to the rational design of mutually interacting carbon dots for a better control over the resulting assembly structure for studying different biological phenomenon including molecular cytogenetics.

**COLL 367**

**Lipid corona formation from nanoparticle interactions with bilayers**

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Mechanisms of corona formation around nanomaterials remain enigmatic. Here, we provide evidence for spontaneous lipid corona formation that engenders new particle properties without the need for active mixing upon attachment to stationary and suspended lipid bilayer membranes. The mechanism of lipid corona formation can be used to improve control over nano-bio interactions and to help understand why some nanomaterial-ligand combinations are detrimental to organisms but others are not.

**COLL 368**

**Erythrocyte membrane-coated piezoelectric sensor for studying the interactions between nanoparticles and surfaces of red blood cells**

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Nanoparticles can enter the human circulatory system through various routes and attach to red blood cells (RBCs). Such attachment may impact biophysical characteristics of RBCs. Thus, it is crucial to quantitatively determine the attachment probability of nanoparticles on RBCs upon collisions. We have developed an erythrocyte membrane coating on a piezoelectric sensor for such quantitative measurements. Membranes of RBCs were extracted from whole blood and well dispersed. The dispersed membranes were characterized through cryogenic transmission electron microscopy (Cryo-TEM), dynamic light scattering, and zeta potential analysis. The size of the dispersed membrane pieces was 390 ± 90 nm and their zeta potential was -0.40 mV at 1 mM NaCl and 0.2 mM NaHCO₃, pH 7.1. The immobilization of membranes was achieved through deposition on the piezoelectric sensor used in a quartz crystal microbalance with dissipation monitoring (QCM-D) system. The frequency shifts of -26.5 ± 3.6 Hz and the low ratios of dissipation shift to frequency shift (0.72×10⁻⁷ ± 0.12×10⁻⁷ Hz⁻¹) suggests the formation of a thin and rigid membrane layer. Such frequency and dissipation features also indicate that most of the developed coating consists of a single layer of phospholipid bilayers. The complete
coverage of the membrane layer on the sensor was verified through deposition experiments of polystyrene nanoparticles. The surface morphology of the membrane coating was characterized via atomic force microscopy in liquid. Immunofluorescence microscopy was conducted on the erythrocyte membrane coating after western blotting for characterizing the distribution of proteins expressed on the surface of RBCs. The results showed that the RBC surface proteins were evenly distributed in the membrane coating. The attachment probability of a model nanoparticle, hematite nanoparticle, on the erythrocyte membrane was obtained in 1 mM NaCl at pH 5.1, using a well-established methodology. The attachment of other types of nanoparticles will also be discussed.

COLL 369

Polysaccharide coated nanoparticles for biological detection

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Carbohydrates are ubiquitous in nature. They play important roles in many biological functions. In this talk, we present our work in combining biological recognition of a polysaccharide, i.e., hyaluronan (HA), with the properties of magnetic nanoparticles for the detection of vascular inflammation and atherosclerosis. Cardiovascular diseases, often associated with inflammation and atherosclerosis, are the leading cause of death and disability in the world. Despite the significant progress in recent years, there remain large unmet needs to detect vulnerable atherosclerotic plaques, which are prone to ruptures subsequently causing heart attacks and strokes. CD44 is a cell surface receptor, which has been shown by multiple studies to promote atherosclerosis by mediating inflammatory cell recruitment and vascular cell activation. Moreover, the expression of CD44 is up-regulated more than ten folds at rupture prone vascular sites, thus presenting an attractive target for molecular imaging. HA is a major endogenous ligand of CD44. In order to detect the presence of CD44 in atherosclerotic plaques, we have synthesized magnetic nanoparticles coated with HA. However, significant inflammatory responses were observed when macrophages were incubated with these nanoparticles. Interestingly, we discovered that engineering of the shape of the nanoprobes can significantly reduce the inflammatory properties of the probes. The new nanoprobes have high relaxivities, which are suitable contrast agents for magnetic resonance imaging. The results on non-invasive in vivo detection of atherosclerotic plaques in a clinically relevant model of ApoE knockout transgenic mice aided by these HA functionalized nanoprobes will be presented.

COLL 370

Noncovalent protein coating onto porous nanoparticles to prevent protein corona enhances in vivo therapeutic efficacy
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Nanoscopic delivery vehicles capable of encapsulating drug molecules and releasing them in response to external stimuli are of great interest due to implications in therapeutic applications. Nano-sized Drug delivery system can minimize the unwanted side effects of traditional chemotherapeutic agents and enhance the delivery efficacy. However, translating nanoparticle-based agents into clinical applications still remains a challenge due to the difficulty in regulating interactions on the interfaces between nanoparticles and biological systems. Here, we present a targeting strategy for nanoparticles incorporated with a supramolecularly pre-coated recombinant fusion protein in which HER2-binding affibody combines with glutathione-S-transferase. Once thermodynamically stabilized in preferred orientations on the nanoparticles, the adsorbed fusion proteins as a corona minimize interactions with serum proteins to prevent the clearance of nanoparticles by macrophages, while ensuring systematic targeting functions *in vitro* and *in vivo*. This study provides insight into the use of the supramolecularly built protein corona shield as a targeting agent through regulating the interfaces between nanoparticles and biological systems.

COLL 371

**Aluminum nanostructures with strong visible-range SERS activity for versatile micropatterning of molecular security labels**

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The application of aluminum (Al)-based nanostructures for visible-range plasmonics, especially for surface-enhanced Raman scattering (SERS), currently suffers from inconsistent local electromagnetic field distributions and/or inhomogeneous distribution of probe molecules. Herein, we lithographically fabricate structurally uniform Al nanostructures which enable homogeneous adsorption of various probe molecules. Individual Al nanostructures exhibit strong local electromagnetic field enhancements, in turn leading to intense SERS activity. The average SERS enhancement factor (EF) for individual nanostructures exceeds 104 for non-resonant probe molecules in the visible spectrum. These Al nanostructures also retain more than 70% of their original SERS intensities after one-month storage, displaying superb stability under ambient conditions. We further achieve tunable polarization-dependent SERS responses using anisotropic Al nanostructures, facilitating the design of sophisticated SERS-based security labels. Our micron-sized security label comprises two-tier security features, including a machine-readable hybrid quick-response (QR) code overlaid with a set of ciphertexts. Our work demonstrates the versatility of Al-based structures in low-cost modern chemical nano-analytics and forgery protection.
Degradation of protein coronas exposed to proteolytic environment of pancreatic tumor cells

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Gold nanoparticles have attracted attention in cancer research as theranostic platforms because their surface can be easily functionalized with biomolecules for drug delivery, gene therapy and specific accumulation at the tumor site. However, nanomaterials change their surface composition when exposed to biological fluids such as blood or serum, resulting in a protein corona which can hinder their function as therapeutic or diagnosis tools. Tumor microenvironments contain high concentrations of proteases, and protease activity can impact the properties of the protein coronas around NPs. In cell culture experiments using PANC1 cells, we measure the time dependent degradation of protein coronas attributed to proteolytic activity of this aggressive pancreatic ductal adenocarcinoma (PDAC) cell line. In addition, we vary the protein corona composition to modulate the degradation rate. Overall, the impact of the protease on protein coronas is complex and involves both exchange and degradation.

COLL 373

Combination of SERS and fluorescence for detection and/or characterization in biological systems

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Dual-mode optical platforms combining fluorescence (or metal-enhanced fluorescence, MEF) and surface-enhanced Raman scattering (SERS) signals into a single probe are emerging as powerful sensing analytical tools, especially in biomedical applications. SERS–fluorescence encoded particles (SFEPs) combine the unique advantages of fluorescence spectroscopy for the rapid read-out over a large area with the high-level of multiplexing and specificity of SERS. This review aims to provide a detailed summary and a critical discussion on the developments of these materials. This will start by highlighting fundamental aspects of the two techniques, then presenting their main building units and corresponding assembling designs and, finally, providing illustrative examples of potential applications.

COLL 374

Quantitative super-resolution imaging of self-assembled nanocarriers via spectroscopic single molecule localization microscopy (sSMLM)

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Self-assembled nanoparticles have great potential for use in bioimaging, diagnostics, and controlled drug delivery applications. Though electron microscopy techniques have greatly enhanced our understanding of the structures of these nanoparticles tracking, quantification, and characterization of these nanoparticles under biological conditions remains poorly understood. Fluorescence microscopy offers the opportunity to visualize these particles in biological samples, however, these nanoscale structures are obscured by the optical diffraction limit. In this study, we utilize spectroscopic single-molecule localization microscopy to image polymersomes (200 nm nanocarriers) assembled from poly(ethylene glycol)-bl-poly(propylene sulfide) (PEG-bl-PPS), where PEG is hydrophilic and PPS is hydrophobic, both immobilized on surfaces and in cells. Taking advantages of a solvatochromic dye-Nile Red (NR), we can distinguish the individual polymersomes based on the unique single-molecule spectral signature of NR when it interacts with polymersomes. Using this property, we can identify the polarity changes associated with polymersome nanoenvironment against the aqueous solutions or intracellular organelle membranes in which NR transiently binds. Therefore, the size distribution and intracellular localizations of polymersomes can be unambiguously quantified using sSMLM, even in highly heterogeneous environments. Ultimately, we anticipate the quantitative super-resolution imaging capability offered by sSMLM will provide an unprecedented solution towards assessing how modifications to the size, surface chemistry, shape, charge, and other properties affect nanoparticle uptake by different endocytosis pathways and cell types.

COLL 375

Synthesis of highly brilliant SERS-encoded nanoparticles: Plasmonic core-satellites structures

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The use of SERS encoded nanoparticles (SEPs) is becoming a powerful method to solve analytical problems in complex media such as biological fluids, due to their high-throughput screening, multiplexing capabilities, and large surface area for bioconjugation. In general, SEPs are made using a plasmonic core with a SERS encoding agent, and a protective layer which allows the attachment of biorecognition elements meanwhile preventing SPEs degradation. However, although these SEPs composed of single plasmonic particles are desirable because of their homogeneous SERS signals.¹ Their efficiency is limited because they cannot form electromagnetic hot spots. Thus, hindering their applicability to other more demanding applications in which acquisition time or spatial resolution are of paramount importance. To solve this problem improving SERS efficiency and consistent signals meanwhile keeping an
appropriate SEP size for biological applications, the development of encoded core-satellites structures is of particular importance because they can concentrate a dense collection of symmetrically arranged hot-spots in a small volume. Herein, we present a synthetic approach that produces homogeneous core-satellite SERS encoded particles with minimal interparticle gaps (< 2-3 nm) and maximum particle loading while positioning the encoding agents at the gaps which have a size range of ca. 100 nm. Moreover, cores of different materials (Au and Ag) and different shapes were produced (Figure 1). These materials present an outstanding optical performance with homogeneous enhancement factors over 4 orders of magnitude as compared with classical SERS encoded particles which allows them for their use as single particle labels.

Figure 1. Core-satellites structures with different core shapes.

COLL 376

Using single-particle spectroscopy to probe nanoparticle uptake by mammalian cells

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Nanoparticles (NPs) are attractive candidates for a variety of biomedical applications, particularly as vehicles for targeted drug delivery and as contrast agents for a variety of imaging techniques. The design of improved materials for any such applications would benefit from detailed studies into how NPs interact with target organ systems at the cellular level. While there have been numerous studies into the roles that NP size, shape, surface chemistry, etc. play in cellular uptake, these studies typically rely on analytical methods which cannot differentiate NPs which are internalized from those simply adhered to the cellular membrane and/or probe the aggregation state of the NPs.
in question. Presented here are results from studies employing single NP spectroscopy as a tool for detailed probing of NP uptake. Au NPs of varying geometries with consistent surface chemistry were synthesized and their uptake by HeLa cells was investigated. The observed optical responses of individual nanostructures demonstrate otherwise stable NPs selectively aggregate when brought into contact with cells. Additionally, optical studies will be discussed which suggest a majority of NPs in this prototypical model system are not internalized, but remain in partially-wrapped states.

**COLL 377**

TiO$_2$ nanoparticles, in the absence of light, oxidize the protein corona leading to an oxidative stress response in cells

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Titanium dioxide nanoparticles (TiO$_2$ NPs) are widely used in commercial and industrial applications. Our previous studies observed an oxidative stress response in cells following a 24 hr incubation with TiO$_2$ NPs, in the absence of light, at low, sub-cytotoxic, concentrations of NPs. Understanding the underlying mechanism of “dark” TiO$_2$ NP-mediated oxidative stress is important as most human interaction with TiO$_2$ NPs takes place in the dark. For example, in the lung following inhalation of TiO$_2$ NPs by factory workers. We used a series of cell-free reactive oxygen species (ROS) assays to characterize ROS production by the TiO$_2$ NPs in the absence of light. A terphthalic acid assay detected hydroxyl radicals and nitro blue tetrazolium assay detected superoxide. EPR spectroscopy also demonstrated the presence of ROS. Amplex Red assay for H$_2$O$_2$ was negative. This ROS generation is correlated with TiO$_2$ NP surface defects, experimentally modulated through surface passivation and plasma treatment. The ROS produced by the TiO$_2$ NPs oxidizes the corona of serum proteins that adsorb on the NP surface, detected as an increase in protein carbonyl content. The oxidized protein triggers an oxidative stress response in cells, observed as changes in the expression of the peroxiredoxin family of anti-oxidant enzymes, detected with PCR and western blot. Our most recent experiments reveal that TiO$_2$ NPs, in the absence of light, lead to changes in global DNA methylation and histone methyl transferase activity, suggesting an epigenetic response to these NPs.

**COLL 378**

Nitroxide-liquid crystal nanoparticle conjugates for the protection of cells against reactive oxygen species
Abstract. Reactive oxygen species (ROS) are highly active chemical reagents that oxidize lipids, proteins, and nucleic acid in cells. Under normal circumstances, ROS play an important role as secondary messengers involved in cellular signaling. However, elevation of ROS levels due to intracellular overproduction or extracellular exposure can cause oxidative stress in cells, which is responsible for irreversible damage and disease. To address this, many strategies have been implemented to neutralize excessive ROS including the administration of conventional antioxidants and ROS scavengers. These approaches, however, in general, fail to achieve the desired efficiency because of the limited cellular uptake of the low-molecular-weight ROS scavengers such as nitroxide derivatives. Recently, nanoparticle (NP)-mediated delivery of ROS scavengers has received attention as the small NP carriers can be loaded and delivered into cellular/subcellular locations. In this study, we have formulated a nitroxide derivative, 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO), that is conjugated to the surface of liquid crystal NPs (LCNP-TEMPO) that can preferentially bind to the plasma membrane and protect the cells from excessive exposure to ROS sources (e.g., hydrogen peroxide). The ability of LCNP-TEMPO to protect cells from intracellular or extracellular exposure of ROS will be discussed.

COLL 379

Ligand dynamics and chemistry on plasmonic nanoparticle surfaces: Insights from plasmon-enhanced spectroscopy

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This presentation focuses on the dynamic interactions between surface-capping ligands and plasmonic nanoparticle surfaces. The interfacial adsorption, desorption, and exchange behaviors of capping ligands on textured nanoparticle surfaces exhibit phenomenal site-to-site variations essentially dictated by the local surface curvatures and surface atomic coordinations, resulting in heterogeneous thermodynamic and kinetic profiles remarkably more sophisticated than those associated with ligand binding to atomically flat surfaces of planar substrates. We use surface-enhanced Raman scattering (SERS) as a plasmon-enhanced spectroscopic tool with unique time-resolving and molecular fingerprinting capabilities to quantitatively correlate the interfacial ligand dynamics with detailed molecular structures in real time under a diverse set of ligand adsorption, desorption, and exchange conditions at both equilibrium and non-equilibrium states. The time-resolved SERS measurements allow us to gain mechanistic insights into the effects of nanoscale surface curvature on the binding affinity, cooperativity, structural ordering, and the adsorption/desorption/exchange dynamics of 3 types of ligands, including aromatic thiols, isocyanides, and diazomium compounds on colloidal metallic nanoparticles. The
insights gained from the SERS results provide an important knowledge framework for us to fully understand the interfacial chemistry and photochemistry of ligand molecules on locally curved nanoparticle surfaces.

COLL 380

Commercialization of gold nanoshells

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Over 20 years ago, gold nanoshells, a seminal plasmonic nanostructure, was invented in the laboratory of Dr. Naomi Halas. The unique optical properties of gold nanoshells has led to a wide variety of scientific research and applications. By controlling the size of the core and the thickness of the gold shell, the peak plasmonic resonance of gold nanoshells can be shifted across the visible and into the infrared region of the electromagnetic spectrum. Nanoshell geometry also impacts the relative contribution of scattering and absorption of individual nanoshells, and by selecting specific core diameters and shell thicknesses, the optical properties can be optimized for applications that range from molecular diagnostics to cancer therapies. Scaled manufacturing of nanoshells for production under ISO 13485 and cGMP presents additional technical challenges that must be overcome for nanoshells to be incorporated into products with global markets. While the commercialization of new materials is challenging and time consuming, the imminent release of a number of products that leverage the novel properties of gold nanoshells demonstrates that plasmonic nanostructures will continue to be an important component of nanotechnology commercialization.
DNA-mediated assembly provides the opportunity to chemically program the structure of nanoparticle-based materials with sub-nanometer precision. Such structural control has accelerated the discovery of new materials with previously unattainable functionalities such as reconfigurability and stimuli responsivity. While most nanoparticle based materials have utilized highly symmetric particles, the use of anisotropic building blocks, which provide directionality to the DNA bonds through their facets, enables enhanced structural complexity and can give rise to unexpected properties. Specifically, anisotropic colloidal crystals assembled from DNA-functionalized, low symmetry nanoparticles can modulate the phase or path of light due to differences in refractive indices along the different crystallographic axes. Such colloidal crystals are, therefore, potentially useful as optical elements in micro-optical systems. Towards the efficient discovery and design of materials with novel functions, a theory-driven platform has been developed to study the relationship between lattice symmetry and photonic stop band properties. Moreover, a template-based assembly strategy, which enables the precise and arbitrary arrangement of nanoparticle building
blocks on surfaces, further expands the structural control of the DNA-mediated nanoparticle assembly platform. Studies on these systems will provide insight into structure-function relationships between structural parameters and optical responses, thus enabling the fabrication of hierarchical metamaterials with specific and tunable outputs.

**COLL 382**

**Correlating carrier density and emergent plasmonic features in Cu$_{2-x}$Se nanoparticles**

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Recently, a wide variety of new nanoparticle compositions have been identified as potential plasmonic materials including earth-abundant metals such as aluminum, highly doped semiconductors, as well as metal pnictides. For semiconductor compositions, plasmonic properties may be tuned not only by nanoparticle size and shape, but also by charge carrier density which can be controlled via a variety of intrinsic and extrinsic doping strategies. Current methods to quantitatively determine charge carrier density primarily rely on interpretation of the nanoparticle extinction spectrum, as well as detailed knowledge of structure-dependent electronic properties, such as the dielectric constants of both the material and surrounding medium (which may or may not include particle ligands). However, this interpretation can be complicated by ambiguity concerning particle structure, and/or convoluted by factors such as particle ligands, size distribution and aggregation state. Therefore, alternative methods to quantify charge carrier density may be transformational in the development of these new materials and would facilitate previously inaccessible correlations between particle synthetic routes, crystallographic features, and emergent optoelectronic properties. Here, we report the use of $^{77}$Se solid state nuclear magnetic resonance (NMR) spectroscopy to quantitatively determine charge carrier density in a variety of Cu$_{2-x}$Se nanoparticle compositions and correlate this charge carrier density with particle crystallinity and extinction features. Importantly, we show that significant charge carrier populations are present even in nanoparticles without spectroscopically discernible plasmonic features and with crystal structures indistinguishable from fully reduced Cu$_2$Se. These results highlight the potential impact of the NMR-based carrier density measurement, especially in the study of plasmon emergence in these systems (i.e., at low dopant concentrations).

**COLL 383**

**From the beaker to an engineering platform: Scale-up, functionalization, and assembly of plasmonic nanoparticles**
Efficient focusing of optical fields at the nanoscale holds immense potential for sensing, photodetection, spectroscopy, and optical information processing. Metallic nanorods and their assemblies are a promising platform due to their intense light-matter interactions, with an optical cross-section greater than the particle volume. Transitioning this potential to applications however requires integrated development of cost-effective, scalable, and sustainable synthesis methods for high precision products, generalizable functionalization strategies that ensure colloidal stability, and high-rate processing that provides spatially ordered arrays with macroscopic alignment. Through a refined understanding of the growth mechanism, we will discuss innovative synthetic strategy of 100-fold, non-volumetric, scale-up of AuNRs that preserves independent control of volume, length and aspect ratio, and provides high quantity products (> grams) with higher-order multipole resonances and absorption/scattering cross-sections approaching theoretical limits. Polarity inversion of the ligand layer via precise control of surfactant concentration enables phase transfer to organic solvents and facilitates the ligand exchange resulting in significantly increased grafting density of polymer grafted nanorods and the formation of C-Au linkages that substantially enhances interface stability. 100+ nM solutions of the later affords rapid (~10s), large area (>cm²), blade coating of ordered monolayer films, whose optical response is tuned by processing conditions and polymer graft molecular weight. Post-processing, such as by laser reshaping, results in voxelated films from a single feedstock. Continual understanding of synthetic and assembly mechanisms is crucial to using such integrated platform technologies for the manufacturing of compact sensors, optical modulators and specialty coatings.

COLL 384

Quantification of the optical properties of colloidal nanoparticles in solutions: Challenges and opportunities

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Colloidal nanoparticles, due to their large sizes, are all relatively strong light scatterers in comparison to small chemical reagents in solutions. Many photoactive nanoparticles are also photon absorbers and emitters. Experimental quantification of the fundamental optical constants of colloidal nanoparticles in terms of their photon absorption, scattering, and emission cross-sections are critical for developing a mechanistic understanding of the correlation between material optical properties and its structural parameters including sizes, shapes, and chemical compositions. Such information holds to key for rational nanoparticle design and applications. However, experimentally decoupling the complex interplay of material photon absorption, scattering, and emission is challenging with existing spectroscopic methods. Introduced in this talk is
the recent polarized resonance synchronous spectroscopic (PRS2) technique for evaluation of the optical activities of colloidal nanoparticles in solutions. The model nanoparticles includes polystyrene nanoparticles that are approximately pure light scatterers with no significant photon absorption and emission in the UV-vis region, plasmonic gold and silver nanoparticles that are simultaneous photon absorbers and scatterers with no significant emission, and fluorescent quantum dots that are simultaneous absorbers, scatterers, and emitters. Besides quantification of nanoparticle photon absorption, scattering, emission cross-sections, and scattering and fluorescence depolarization, PRS2 application for in-situ non-invasive monitoring nanoparticle size and shape variations will also be discussed.

COLL 385

Synthesis and characterization of perovskites for energy applications

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With the ultimate goal of finding simultaneously cost-effective, more earth-abundant, and high-performance alternatives to commercial alternatives for electrocatalysis and solar energy conversion, this presentation will highlight synthetic advances in the use of perovskites as (i) electrocatalysts and (ii) light harvesting materials. In the first case, perovskite metal oxides are promising as versatile functional replacements for platinum-group metals, because of their excellent conductivity, overall resistance to corrosion, good proton transport properties, and potential for interesting acidic surface chemistry, all of which contribute to their high activity and reasonable stability, especially within an alkaline electrolytic environment. In the second case, we have focused on structures associated with an ABX$_3$ structure, incorporating species such as a larger cation A, a smaller cation B, and an anion X. These organometallic halide perovskites have shown very promising performance for energy conversion applications with measured power conversion efficiencies (PCE) routinely surpassing 20%. Several factors appear to play a role in this behavior, with one of the most important ones ascribed to the capability of tuning bandgaps through externally controlled variables such as chemical composition.

COLL 386

Perovskite colloidal quantum wells: Self-assembly and physics

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Colloidal perovskite quantum dots are emerging as one of the most promising candidates for next-generation optoelectronics. To make optoelectronic devices, it is required to control self assembly and the photophysical properties of the self-assembled superlattices. In this talk, I will be focused on the superlattices of perovskite colloidal quantum wells (CQWs), based on our recent progress in this field. Our findings reveal three new physical properties that have never been observed in typical quantum dot
solids, including: (i) the aggregation-induced emission characteristics, (ii) the inhibited Forster resonance energy transfer (FRET) between neighbor wells, and (iii) the emission directionality. I will cover the physics and the implications of the new physical mechanisms.

COLL 387

Sonochemical synthesis of polymorphic lead halide perovskite microcrystals in polar solvents

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Lead halide perovskites (LHPs) (ABX\textsubscript{3}, A=Cs\textsuperscript{+}, CH\textsubscript{3}NH\textsubscript{3}\textsuperscript{+}, B=Pb\textsuperscript{2+}, X=Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-}) have emerged as one of the most promising materials for optoelectric applications. LHPs are typically assembled in non-polar solvents to protect the materials from degradation. Here, we present colloidal sonochemistry as a new method to synthesize LHP microcrystals in polar solvents (Fig. A). Our mechanistic study suggests that ultrasonication of a precursor solution creates unstable supersaturation to generate spontaneous nucleation and growth of LHPs. Using CsBr and PbBr\textsubscript{2} precursor salts in 1:1 ratio in DMF, sonochemistry allowed us to produce billions of high-quality CsPbBr\textsubscript{3} microcrystals in 2 minutes (Fig. A). Different concentrations and relative ratios of the precursors yielded various types of products, such as single-phase Cs\textsubscript{4}PbBr\textsubscript{6} microparticles, dual-phase CsPbBr\textsubscript{3}-in-Cs\textsubscript{4}PbBr\textsubscript{6} microparticles in disc, hexagonal plate, and rhombus shapes, and dual-phase CsPbBr\textsubscript{3}-in-CsPb\textsubscript{2}Br\textsubscript{5} microparticles with various morphologies. TEM imaging revealed that the dual-phase composites have CsPbBr\textsubscript{3} nanocrystals (NCs) embedded in Cs\textsubscript{4}PbBr\textsubscript{6} or CsPb\textsubscript{2}Br\textsubscript{5} matrices (Fig. B). The typical size of CsPbBr\textsubscript{3} NCs was 3-5 nm in Cs\textsubscript{4}PbBr\textsubscript{6} and 10-20 nm in CsPb\textsubscript{2}Br\textsubscript{5}. High-resolution transmission electron microscopy images reveal their internal lattice arrangements with reasonable facet matching between CsPbBr\textsubscript{3} and matrices.
Fig. A. Schematic of the sonochemical synthesis using ultrasonication of AX and PbX₂ (A=Cs⁺, CH₃NH₃⁺, X=Cl⁻, Br⁻, I⁻) in DMF, with relative concentration of a:b (left). A 250-mL solution in DMF containing about 2 billion CsPbBr₃ microcrystals (right). B. TEM image of a dual phase Cs₄PbBr₆/CsPbBr₃ microdisc (left) and a dual phase CsPb₂Br₅/CsPbBr₃ cuboctahedron (right).

**COLL 388**

**Boron cluster building blocks for the development of hybrid materials**

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200 years of research with carbon-rich molecules have shaped the development of modern chemistry. Research pertaining to the chemistry of boron-rich species has historically trailed behind its more distinguished neighbor (carbon) in the periodic table. Most importantly, a potentially rich and, in many cases, unmatched field of using boron-rich clusters in materials science remains fundamentally underdeveloped. Our work is devoted towards examining several basic concepts related to the functionalization of polyhedral boron-rich clusters and their use as unique building blocks for materials with applications ranging from catalysis to modulating protein-biomolecule interactions.

These clusters are particularly interesting since they can be regarded as three-dimensional (3D) analogs of benzene. The unique chemical and physical properties of these species such as rigidity, inertness, and 3D aromaticity, allows one to access a set of properties not normally available in carbon-based chemistry. In the past several years we demonstrated how these clusters can be used to create a new class of organic light emitting diode materials, extremely powerful photo-oxidant reagents for polymerization, unique building blocks for stabilization of surfaces and atomically-precise nanoparticle surrogates featuring improved stabilities in biological media. My presentation will focus on several of these recent developments highlighting new directions for these clusters as they apply to new potential applications in nano- and materials sciences.
Novel nanohybrids of chemically active boron based nanosheets with gold nanoparticles and graphene: Assembling mixed dimensional heterostructures in solution

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The discovery of graphene inspired ground-breaking research in the field of two-dimensional materials. The current decade, however, has seen the 2D materials landscape evolving beyond graphene. Boron, carbon’s neighbor in the periodic table, has been seeking significant attention regarding its existence in planar forms analogous to graphene. 2D Boron has been in the limelight since 2015 when the first reports on the bottom-up synthesis of ‘borophene’ nanosheets were published. Although several theoretical studies predict quasi-planar forms of boron, their experimental realization remains challenging. The apparent absence of a suitable layered 3D precursor has precluded the top-down synthesis of boron sheets by exfoliation. We present a fundamentally new perspective to this growing science of 2D Boron by proposing to use layered metal borides towards the exfoliative synthesis of boron-based nanosheets. Metal borides are layered compounds constituted of (graphene-like) honeycomb planes of boron sandwiched between hexagonal layers of metal atoms. We recently developed a chemical exfoliation strategy in which organic chelators selectively extract metal ions from layered borides in an aqueous medium. This causes delamination of boride crystals into few-layer-thick boron-based nanosheets. Detailed chemical characterization indicated that the nanosheets possessed hydride, hydroxy and oxy based functional groups. The presence of borohydride groups confers a unique chemically active character to the nanosheets to reduce several organic and inorganic molecules. Mixing these nanosheets with gold salt results in a spontaneous formation of ultra-small gold nanoparticles that subsequently anchor onto the nanosheets and form mixed-dimensional (0D-2D) heterostructures in solution. This process neither requires any reducing-stabilizing chemical nor an external inducing aide like sonication, electrochemical or thermal treatment. These nanosheets can also reduce graphene oxide to reduced graphene oxide subsequently forming quasi-2D boron-carbon nanohybrids. We present for the first time the possibility of using a boron-rich 2D material as a nanoscale reducing agent. The concurrence of reducing nature and planarity makes these nanosheets intriguing alternatives over conventional reductants. A wide range of possibilities can be realized by employing these as nanoscale reagents, and as building blocks towards assembling heterostructures with other low-dimensional systems.
Influence of nanoparticle dimensionality on rates of electron transfer between semiconductor nanoparticles

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Recent advances in nanoparticle synthesis have presented scientists with the opportunity to control not only nanoparticle size and composition, but also morphology and dimensionality. Among these advances, colloidal, two-dimensional nanocrystals known as nanoplatelets have emerged, which display exceptionally narrow photoluminescence linewidth and large absorption cross-sections that arise specifically as a result of their dimensionality. However, while extensive studies have led to an understanding of how electron transfer rates scale with nanoparticle size, analogous studies relating rates of electron transfer to nanoparticle dimensionality are lacking. Here, we study electronic interactions in films containing mixtures of zero- or two-dimensional nanostructures (quantum dots or nanoplatelets, respectively) with constant driving force and nanoparticle separation, achieved via the use of isoenergetic nanoparticles and identical capping ligands. Electron transfer is observed in all of the examined mixtures, regardless of the particle dimensionality, and characterized via static and time-resolved photoluminescence, as well as transient absorption spectroscopy. Rates of electron transfer for different combinations of dimensionalities in dilute and concentrated films reveal that dimensionality does, in fact, impact rates of electron transfer, with films containing nanoplatelets exhibiting faster charge separation rates. This novel insight into how dimensionality affects exciton dynamics has implications in the design of photocatalysts and optoelectronic devices such as photovoltaics, as the appropriate selection of nanoparticle dimension can potentially boost device efficiencies.

COLL 391

Colloidal semiconductor CdS magic-size clusters: Thermally induced reversible structural isomerization

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Here, we report the first pair of structural isomers identified for colloidal nanocrystals which exhibit thermally-induced reversible transformations. The two isomers are CdS magic-size clusters (MSCs) exhibiting sharp absorption peaks at 311 nm and 322 nm. We show that their thermally-induced interconversions follow first-order unimolecular reaction kinetics. We anticipate that our findings on structural isomerism should stimulate attention towards solid-solid transformations and advanced design and synthesis of functional nanomaterials for a diversity of applications enabled by structural transformations.
SnGe alloys: Full compositional range at nanoscale

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Germanium (Ge) is one of the extensively studied semiconductors possessing higher absorption coefficient and carrier mobilities than silicon. Recently, it has also been realized that Ge is well suited as an anode for Li or Na ion batteries. However, inherently inefficient light absorption of Ge and large volume change during lithiation/delithiation process impedes its further use in optical and energy storage applications. Although alloying of Ge with Sn was concluded to be potentially beneficial to address both issues, very low solubility and large lattice mismatch between Ge and Sn made it challenging to prepare SnGe alloys with any significant degree of element mixing. We have developed a synthetic approach to Sn\textsubscript{x}Ge\textsubscript{1-x} nanoalloys with almost entire compositional range (with Sn content up to 95\%) while still retaining the cubic phase of the material. Some insights into the alloying mechanism have been elucidated experimentally with support from DFT calculations. As synthesized, the nanoalloys are stable up to 200°C, after which the phase segregation sets in. Controlled sulfidization of the nanoalloy surface increases thermal stability of particles up to 500 °C. Sulfur treatment also enables the ligand exchange on the particle surface, thereby rendering particles processable for the preparation of thin films with close interparticle contacts. The synthesis, mechanistic studies and properties important for photovoltaic and energy storage applications will be discussed.

Self-assembly of CdSe nanoplatelets into twisted threads

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Colloidal CdSe nanoplatelets are light emitting materials which exhibit outstanding optical properties\textsuperscript{1,2}. They are considered to be excellent candidates for many applications in nanotechnology due to their fast fluorescence lifetime and their small spectral linewidth. One of the current challenges is to self-assemble these colloidal quantum wells into large ordered structures to control their collective optical properties. We describe a simple and robust procedure to achieve controlled face-to-face self-assembly of CdSe nanoplatelets into micron-long polymer-like threads made of up to
∼1000 particles. These structures are formed by addition of oleic acid to a stable colloidal dispersion of platelets, followed by slow drying and re-dispersion. We could control the average length of the CdSe nanoplatelet threads by varying the amount of added oleic acid. Since they are composed of a single platelet in their lateral dimension, these structures are highly flexible. Furthermore, they continuously break and reform in solution. In some cases, we show that the threads twist and yield chiral structures with a given handedness. We propose a mechanism based on the release of stress imposed by the ligand at the surface of the platelet to explain this twisting phenomenon.

**COLL 394**

**Self-assembly of aryl halides for various degrees of dehalogenation**

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Aryl halides are among the most important molecular precursors for on-surface synthesis. Their dehalogenative coupling – so called surface-assisted Ullmann-type coupling – represents a unique synthetic route for the bottom-up fabrication of extended low-dimensional covalent nanostructures that exhibit all benefits of strong carbon-carbon linkages.
Organometallic templating has proven an invaluable tool for improving the notoriously low structural quality of 2D covalent networks. Structural equilibration in the organometallic stage, where dehalogenated monomers form reticulated networks based on organometallic carbon-metal-carbon linkages, can promote the on-surface synthesis of regular and defined covalent networks. In these favorable cases, the order generated in the organometallic networks was transferred to the final covalent product by a thermally activated isostructural conversion. On the one hand, studying organometallic self-assembly is per se rewarding, since an advanced understanding of its mechanisms could contribute to further push its limits. On the other hand, the partial dehalogenation, as typically observed on silver surfaces, gives rise to new modes of supramolecular self-assembly, where both the split off and subsequently chemisorbed halogens and organometallic metal atoms represent dominating interaction sites.

In this contribution, we will discuss self-assembly of aryl halides on surfaces for various degrees of dehalogenation ranging from fully halogenated to fully dehalogenated. Moreover, we will demonstrate, how a detailed analysis of the stereochemical distribution of dehalogenated sites holds the potential for elucidating fundamental aspects of surface-assisted dehalogenative couplings.
Porphyrrins are ideally suited to the growth of functional molecular networks. Structural versatility coupled with desirable optical and chemical properties have seen porphyrins find applications in areas including dye-sensitised solar cells, photodynamic therapy and the design of electro-catalytic surfaces. This talk will present two aspects of our research into the growth of two-dimensional porphyrin networks: (1) the formation of imine stabilised 2D covalent-organic frameworks and their post-growth chemical modification; and (2) the use of nucleobase functional groups to control the complex self-assembly of multi-component porphyrin networks. The growth of 2D covalent-organic frameworks (2D-COFs) via imine formation is a widely applied technique. In the first half of my talk I will present results showing the formation of highly ordered monolayer and bi-layer 2D-COFs grown using either freebase or metal containing tetra(4-aminophenyl)porphyrins. The resulting 2D-COF layers were characterised using scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). A potential limiting factor to the application of 2D-COF thin-films is the low stability of imine bonds with respect to hydrolysis. We demonstrate a post-growth chemical modification approach that reduces imines to secondary amines. This process dramatically increases the stability of the framework layers while maintaining the highly ordered structure of the 2D-COF. In the final part of my talk I will present the synthesis and 2D self-assembly of nucleobase functionalised porphyrins. Tetra(phenylthymine) zinc porphyrin (Zn-tetra-TP) and tetra(phenyladenine) porphyrin (tetra-AP) have been synthesised and their self-assembly at a liquid-solid interface investigated using STM. Self-assembly of mono-component mixtures of these porphyrins produces an open porous network for Zn-tetra-TP, and a more close-packed network for tetra-AP. However, mixtures of the two components self-assemble into a structure with \( p4 \) symmetry consisting of alternating Zn-tetra-TP and tetra-AP molecules in a chessboard type pattern. Molecular mechanics (MM) simulations based on drift corrected STM images suggest hydrogen bonding in the mixed networks is in the form adenine-thymine (ATAT) quartets, see figure 1. This result opens up the possibility of using selective interactions between nucleobase functional groups to drive the 2D self-assembly of complex 2D porphyrin networks.

COLL 396

On-surface synthesis: strategies towards the targeted products

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On-surface synthesis has attracted intensive attention in recent years due to its tremendous potential in fabrication of novel functional molecules and low-dimensional nanomaterials. In response to the demand for the synthesis of high-quality nanostructures, many efforts have been made to steer the reaction pathway and improve the chemo-/regio-selectivity, typically by smart precursor design and substrate templating effect. However, the precise control of the complex on-surface reactions with multiple pathways still remains challenging because only very few parameters can be tuned in the UHV environment in contrast to the traditional wet chemistry where various
catalysts can be employed. In this presentation, I will report three typical coupling reactions, namely Ullman, Glaser and Sonagashira couplings, on the Ag(111) surface by using a single precursor molecule, i.e., 1,1'-biphenyl,4-bromo-4'-ethynyl (BPBE). By utilizing thermal stimuli procedures and kinetic strategies, the reactions of BPBE on Ag(111) can be efficiently steered towards the formation of cis-enediyne trimer, graphdiyne and graphyne nanowires. The reaction products and mechanism can be monitored and understood by the combination of scanning tunneling microscopy (STM), high resolution X-ray photoelectron spectroscopy (HRXPS) and density functional theory (DFT). I will show that the substrate temperature, annealing procedure, reactant concentration, molecular adsorption, desorption and diffusion all play important roles in the control of on-surface reactions. This work provides a fundamental insight of how to steer complex and multipath on-surface reactions towards the selected target products.

COLL 397

Long-range ordered and atomic-scale control of graphene hybridization by photocycloaddition

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Cycloaddition has been demonstrated to be an effective path to introduce sp² hybridization hence functionalize graphene, yet still presenting considerable challenges. Albeit the diverse methods to enable the reactions, such as heating, long soaking in solution, electric pulse, or tip press, photocycloaddition of graphene has been fairly scarce; nevertheless, its potential merits, such as simplicity, remote controllability, and compatibility with other photo-related techniques, would be desirable for practical applications. As widely demonstrated by theoretical results and experimental observations, cycloaddition favors graphene defects and edges, and has a low probability of occurring on defect-free pristine graphene. Even if the reactions were induced, based on the samples prepared in solution and the globally averaging measurements, it is rather challenging to determine the local reaction sites, or ascertain whether the reaction occurred with the target molecules or impurities. Scanning probe microscopy (SPM) under ultrahigh vacuum (UHV) conditions is more appropriate to addressing these challenges. However, only one successful demonstration of cycloaddition in UHV has been reported, where the reaction was accomplished exclusively on isolated molecules at liquid helium temperature. So far, it has not been possible to realize chemical reactions of graphene with molecular networks nor achieve two-dimensional (2D) order of reaction sites at atomic/molecular scale.

Here, we report a reversible in situ D-A reaction of an extended molecular network placed on a single-layer defect-free pristine graphene sheet, directly visualized by high-resolution scanning tunnelling microscopy and confirmed by ab initio density functional theory calculations, infrared reflection-absorption spectroscopy (IRAS), and Raman spectroscopy. The reaction is triggered by ultraviolet irradiation at room temperature, with the reaction sites being spatially selective and in a 2D long-range order. As the first
example for reaction of graphene with molecular network, this work opens up an efficient and convenient route to fabricate highly precise and long-range ordered electronic matrix of graphene, and may spark considerable enthusiasm to develop diverse fascinating electronic matrixes by the facile chemical reactions of supramolecular networks with graphene for designing and engineering graphene-based optoelectronics devices and microelectronic techniques.

**COLL 398**

**Bottom-up fabrication of atomically precise molecular nanostructures through on-surface reactions**

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The interest in molecular nanostructures on surfaces emerges from their prospective applications in nanoscale electronics, solar cells, energy storage devices, and other fields. Non-covalent intermolecular interactions in molecular self-assemblies facilitate the formation of long-range ordered patterns by usage of molecular recognition. In contrast, the fabrication of long-range ordered two-dimensional covalently-linked networks via on-surface reactions is still a major challenge in ultra-high vacuum owing to the irreversible nature of the covalent bonds.

In my presentation, I will focus on recent high-resolution scanning probe microscopy experiments in combination with density-functional theory about the bottom-up fabrication and electronic properties of atomically precise one- and two-dimensional molecular nanostructures on metals. Thereby, the effect of the flexibility, the symmetry, and chirality of the precursor molecules on the structure formation of covalently-linked molecular structures will be discussed. In particular, I will outline how well-ordered nanoporous 1D and 2D covalent molecular structures, can be fabricated by use of debromination coupling reactions. The narrowing of the band gap from single precursor molecules to the 2D materials due to the extension of the \( \pi \)-system will be shown. Moreover, we found also delocalized electronic states in surface-supported organometallic networks, which benefit from crystallization into large networks upon annealing.

**COLL 399**

**Assemblies and reactions of small carboxylated molecules on metal surfaces: diverse chemical and structural outcomes from simple precursor molecules**

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In the pursuit of applications-targeted materials, the reaction of small molecular precursors on a surface is emerging as an attractive route towards designing 1D and 2D
materials with well-defined chemical and structural properties. For example, the use of extended molecular scaffolds has led to unprecedented control over the growth of graphene nanoribbons on surfaces.[1] In this same vein, we have been systematically studying the use of small, single-ring aromatic precursor molecules as candidates for on-surface materials synthesis. Ironically, these simple molecules exhibit surprisingly complex behaviour under reaction conditions on metal surfaces. Here, I will discuss what we have learned by studying a range of di- and tri-carboxylated pyridine and benzene-based molecules on copper and silver single crystals. Through thermal annealing, we initiate first deprotonation, then decarboxylation of the molecules. We find that the adsorption geometry of the molecules changes significantly as they undergo successive reactions,[2] that molecules in different chemical states can assemble into complex structural motifs,[3] and that maintaining the pyridine ring integrity during decarboxylation may be difficult.[4] We have studied these systems using a range of surface science techniques including photoelectron spectroscopy, near-edge x-ray absorption fine structure and scanning tunnelling microscopy. When combined with density functional theory calculations, these measurements give us well-rounded insight into the challenges inherent in predictive control of on-surface synthesis using small precursor molecules.

**COLL 400**

**Selective activation of chemical bonds in on-surface chemistry**

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The goal of modern synthetic chemistry is to develop ideal new reactions and new methods, to precisely control the chemical reactions and to find more accurate ways of material transformation. In recent years, the preparation of novel molecular materials has attracted much attention in surface science by constructing covalently linked molecular structures through on-surface chemistry. The surface, with its inherent characteristics such as spatial confinement and different adsorption sites, provides an excellent and unique platform for controlling the accuracy of chemical reactions. Here we will set out from a few examples to elucidate our understanding of surface chemical reactions and pathways which are different from conventional reactions. Especially, we will discuss the mechanism how the surface causes the selective breaking and forming the chemical bondws and induce the selective activities of chemical identical groups.

**COLL 401**

**Synthesis and directed assembly plasmonic nanostructures**

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An exquisite sensitivity to the local environment combined with their ability to dramatically concentrate electromagnetic fields makes plasmon-resonant nanoparticles ideal candidates for reporting on their local environment. These properties enable the assembly of both stimulus responsive materials, and the use of metal nanostructures as reporters of their own nucleation, growth, and assembly. In this talk, we explore the synthesis and characterization of hybrid metal/polymer nanostructures, where the polymeric materials can either template the self-assembly of the metals, or direct the synthesis of specific architectures from solution precursors. These studies provide real-time optical probes of the synthesis and assembly state of colloidal nanostructures.

**COLL 402**

**Organizing nanorods end to end**

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Gold nanorods exhibit longitudinal plasmon resonances that can couple if the rods are organized in an end-to-end fashion at close enough distances. Here I will survey work in this area, and describe surface chemistry and assembly approaches to organize gold nanorods in one-dimensional arrays.

**COLL 403**

**In-situ scattering techniques to study synthesis and crystallization processes of colloidal nanocrystals**

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The synthesis of precise nanomaterials is crucial to both advance fundamental knowledge and to fully exploit their peculiar properties. Basic studies on the synthesis of colloidal materials are needed in order to improve current methods for making these precise building blocks. In this talk, recent results on the use of *in-situ* scattering techniques to study these processes will be presented. Novel insights into the role of surfactants and reaction conditions for the growth of precise metallic nanocrystals will be provided. Furthermore, the discovery of crystallization processes occurring during the synthesis process will be discussed, with the opportunity to engineer not only the structure of individual nanocrystals, but also to extend this control to self-assembled materials such as superlattices. This increased knowledge, corroborated by thermodynamic models, is utilized to tune and control the size and composition of colloidal nanocrystals, which are important parameters in their applications in many areas, for example in catalysis.
Templated evaporative self-assembly as a powerful tool for creating functional superstructures and patterns

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Spontaneous assembly of colloidal nanostructures is often viewed as a bottom-up alternative to lithographic techniques when it comes to creating materials with novel collective properties. The intensive research in the past 10-15 years has brought numerous examples of functional superlattices, 3D colloidal crystals, and designed patterns of nanostructures. However, the majority of self-assembly methods suffer from poor reproducibility and limited scale, which often precludes the formation of macroscopically large structures and functional devices. This presentation will focus on the evaporative self-assembly of anisotropic gold nanocrystals and the underlying mechanisms of their colloidal crystallization. In addition, template-assisted evaporative assembly of nanowires, polymers, and collagen fibers into macroscopically-large hexagonal patterns will be discussed.

In situ high-energy XRD studies on the nucleation, growth, and 3D atomic structure of ultrathin Au nanowires in solution

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Despite the intensive interest in thin gold nanowires for a variety of technologically important applications, key details of the mechanism of their formation and atomic-scale structure remain unknown. We synthesized uniform, very long and ultrathin gold nanowires in a liquid-phase environment, and studied their nucleation and growth using \textit{in situ} high-energy synchrotron x-ray diffraction. We will present details from the study and show that the formation of gold nanowires involves the emergence and self-assembly of transient linear gold complexes. We will discuss the mechanism of self-assembly in terms of aurophilic interactions between the complexes and excluded volume effects. We will also show that the resulting nanowires adopt an unusual topologically close-packed structure that is quite different from the fcc structure of bulk gold. Potential applications of the nanowires will be discussed as well.
Understanding the role of soft ligands on nanoparticle assembly using small angle x-ray and neutron scattering techniques

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The role of capping ligands on nanoparticles on their assembly has been extensively studied by many research groups. In the studies, x-ray scattering method has been a key technique to visualize the very details of the assembled structure including the orientation of particles in the superlattice and precise measurement of gap distance and packing fraction, thereby enabling energy calculation. This talk will briefly review small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) methods that we have applied for PbS nanoparticles capped with oleic acid and gold nanoparticles stabilized with CTAB. We will show how SANS measurements help to determine the degree of solvation of the oleic acids on PbS nanoparticles in a mixed solution of good and poor solvents that are toluene and alcohol, respectively. In addition, our recent result on complete 3D reciprocal space mapping of a mesocrystal will be discussed, which reveals defects in the crystals.

Nanoisland deposition on colloidal nanoparticle substrates
Noble metal nanoparticles with nanoisland exteriors are an emerging class of materials with desirable physical and chemical properties. Typically comprised of two or more metals, these materials are a distinct subset of multimetallic core@shell architectures where the shell is comprised of individual metal islands rather than a continuous metal shell. Here, we describe the synthesis and mechanisms of metal nanoisland formation on a variety of noble metal and semiconductor nanoparticle surfaces. We specifically draw connections and distinctions between the driving forces for island growth in thin films and on colloidal nanoparticles. We then build on these trends to identify key chemical parameters that influence the synthesis and optoelectronic properties of core@island nanoparticle motifs.

COLL 408

Protein corona formation on nanoparticles and its effect on interaction with biological membranes

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The interaction between nanomaterials and plasma membranes plays an important role in biological processes. An increasing number of computational and experimental studies have investigated the direct interaction between nanomaterials and plasma membranes. However, once entering physiological media, nanomaterials quickly pick up biomolecules around them and are covered by a biomolecular corona which defines many of their biological outcomes.

To elucidate how this protein corona affects the interplay between nanomaterials and the plasma membrane, we chose polystyrene nanoparticles with various surface charges and coatings, and we studied protein corona formation on these nanoparticles after being incubated in serum. Furthermore, we observed their adhesion to cultured cells as well as cellular uptake. As an artificial platform to mimic plasma membranes, giant unilamellar vesicles (GUVs) were utilized to interpret this interaction. We successfully manufactured GUVs from total lipid extracts of natural organs and investigated the interaction with polystyrene nanoparticles in the presence or absence of protein corona. We found that a protein corona reduced adhesion of nanoparticles onto both biomimetic lipid bilayers and cell membranes. Meanwhile, differences in lipid compositions resulted in varied behaviors in the presence of a protein corona. This study evaluates the capability of artificial lipid bilayers to mimic plasma membranes and provides fundamental insights for the development of drug delivery vehicles.

COLL 409

Substrate specificity of P4-ATPases
The transbilayer distribution of phospholipids across mammalian plasma membranes is generated and maintained by vectoral lipid synthesis, protein-lipid interactions, a thermodynamic barrier to spontaneous transbilayer movement and the action of phospholipid-specific transporters. These ATP-dependent outwardly-directed (fipppase) and cytofacially-directed (flippase) enzymes work in concert to maintain transmembrane phospholipid asymmetry. A subclass of P-type ATPases, the P4-family, include a number of flippases with varied substrate specificity. The plasma membrane P4-flippases ATP8A1 and ATP11C, prefer phosphatidylserine (PS), and to a lesser extent, phosphatidylethanolamine, as optimal substrates. In intact cells, PS transport activity by these proteins is highly selective for the structure of the lipid substrate. Structural modification of the amine, carboxyl, or phosphate groups of PS significantly diminishes transport activity, although N-methyl-PS is transported at rates comparable to PS. Variations in fatty acyl chain length and composition are tolerated, but ester linkages are preferred. While the stereo-chemical configuration of the serine headgroup is relatively unimportant (both L- and D-serine analogs are transported at similar rates), the stereo-chemical configuration of the C2 carbon of the glycerol moiety is critical; the non-natural sn-2,3 isomer is a poor substrate compared to the natural sn-1,2 isomer. This pattern of specificity is also observed for the ATPase activity of purified, reconstituted ATP8A1. In addition, some of these PS analogs, but not all, are effective competitive inhibitors of flippase, and associated ATPase, activity, indicating that they are likely substrates for the same protein. In an effort to identify the molecular determinants of substrate specificity, recent modelling and structural elucidation studies of purified P4-ATPases have revealed potential transmembrane lipid transport pathways, as well as identified amino acid residues that might be involved in substrate selectivity.

COLL 410

Fatty acid flip-flop in lipid membranes

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The process of fatty acid transport across the cellular membrane occurs in three unique steps: adsorption, translocation, and desorption. The adsorption/desorption steps involve equilibrium between the membrane and surrounding media or cytosol while translocation is the movement of the fatty acid from the outer leaflet to the inner leaflet. There are essentially two competing hypotheses regarding fatty acid transport. The first is that the flip-flop of fatty acids through the hydrophobic core of the plasma membrane is the rate-limiting step to transport. In this case of prohibitively slow flip-flop, the invocation of a protein-mediated transport mechanism is necessary to support cell viability. Alternatively, the other hypothesis states the rate of fatty acid flip-flop occurs
rapidly, with desorption being the rate-limiting step to transport through the membrane. This would suggest that a diffusive transport mechanism is sufficient to support the metabolic demands of the cell. The rate and mechanism by which this crossing occurs is poorly understood due to experimental difficulty of determining the rate of fatty acid flip-flop in membranes. Sum-frequency vibrational spectroscopy (SFVS) has been used to determine the rate of stearic acid (SA) flip-flop in planar-supported lipid bilayers (PSLB) composed of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC). In addition to SA flip-flop, the effect of SA on DSPC flip-flop was also examined. SA flip-flop was found to be rapid, but surprisingly, also slows the translocation of DSPC. SFVS measurements of SA flip-flop suggest that desorption is the rate limiting step in fatty acid transport across the cellular membrane.

**COLL 411**

**Consequences of oxidation of plasma membrane lipids**

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The lipid bilayer is a key site for oxidative damage; unsaturated lipids are particularly labile to oxidation. In vitro models have demonstrated that oxidation alters key properties of the lipid bilayer including permeability, morphology, and phase state. However, it remains unclear to what extent oxidation persists in the membranes of living cells, which incorporate mechanisms for preventing oxidative damage and regenerating plasma membrane lipids. Here, we expose cells in culture to a variety of oxidative environments, extract lipids from their plasma membranes, and use lipidomic techniques to quantify the extent of oxidation.

In our previous work, we have shown that at low degrees of oxidation (fewer that 3% of unsaturated lipids oxidized), bilayers demonstrate radically increased permeability to small molecules. This represents a potentially catastrophic compromising of the barrier properties of the plasma membrane. Oxidation is also capable of radically altering the morphology of lipid bilayers, altering the dimensions of lipids in a manner that leads to changes in membrane tension and subsequent pore formation. Similarly, oxidation can lead to processes that inhibit the capacity of lipid bilayers to form high-curvature structures.

To better model modes of oxidative damage to the cellular plasma membrane, we have exposed cells in culture to both chemical oxidation and growth in a high oxygen partial pressure environment. Cell viability was analyzed and lipids were extracted from the cell to assess the mechanical properties and permeability of lipid bilayers constructed from them. Extracted lipids were also subject to lipidomic analysis to clarify the compositional changes that occur in plasma membranes in an oxidative environment.

**COLL 412**
Compositional and biophysical asymmetry in mammalian membrane bilayers

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Cells invest significant energetic resources to maintain a compositional asymmetry between the two apposing leaflets of the plasma membrane (PM), emphasizing the importance of this distribution for cell homeostasis. For example, phospholipid asymmetry produces a negative surface potential on the cytoplasmic PM leaflet, which facilitates binding of positively charged proteins. Despite the central involvement of PM asymmetry in various physiological processes, the distinct, detailed, comprehensive compositions of the PM leaflets are not known, nor is the influence of asymmetric lipid distribution on leaflet biophysical properties. We therefore combined a detailed lipidomic analysis of plasma membrane leaflet compositions with an investigation of leaflet-specific biophysical leaflet properties. In human red blood cell membranes, we describe for the first time the detailed lipidomics of both bilayer leaflets, including a dramatic disparity in lipid acyl chains, with the inner plasma membrane leaflet containing approximately two-fold more acyl chain unsaturations compared to the outer leaflet. Membranes containing highly unsaturated lipids are typically characterized by reduced lipid packing and order compared to those with more saturated acyl chains, suggesting the potential for an order asymmetry in living PMs. Using an environment-sensitive probe (Di4), we indeed observed a large lipid order difference between the two PM leaflets. The outer leaflet is tightly packed, approximately comparable to a liquid ordered “raft” phase. In contrast, the inner leaflet is much more disordered. This phase asymmetry is largely maintained during endocytosis. An analysis of the human proteome revealed that transmembrane proteins have asymmetric shape in their transmembrane domains, but only in organelles which participate in exo- or endocytosis. This asymmetric shape maintains an energetically favourable interaction with the asymmetrically packed membranes, and we conclude that those shapes have co-evolved with the lipid phase asymmetries of living membranes. The function of the observed phase asymmetry remains to be definitively determined, but we speculate that this arrangement is a “best of both worlds”, combining low permeability and high mechanical robustness in the exoplasmic leaflet with high mobility and diffusion in the cytoplasmic leaflet required for dynamic intracellular signaling.

COLL 413

Supported membranes as a platform for dynamic phenotyping of primary human cells: Quantifying the effect of intrinsic and extrinsic factors

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Adhesion, active deformation, and migration of cells are significantly modulated by intrinsic changes of cells such as aging or epigenetic modification as well as extrinsic
factors such as chemokines and drugs. Label-free, "dynamic" phenotyping that quantifies active deformation and motion of cells can complement the commonly used "static" phenotyping relying on multiple immunostaining using high throughput microscopy. The combination of quantitatively functionalized membranes, characteristic spatio-temporal patterns, Fourier space analyses, and theoretical models is a powerful to quantitatively determine the impact of progression of disease, natural chemokine and clinical drugs on the adhesion strength, mode of deformation and migration trajectories of primary human cells.

COLL 414

Physical properties of simple sphingolipids in phospholipid bilayers: Wild, tamed, and caged tigers

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Some of the simplest sphingolipids, namely sphingosine or ceramide are potent metabolic regulators. Each of these lipids modifies in marked and specific ways the physical properties of the cell membranes, in what can be the basis for some of their physiological actions. This presentation is an overview of the mechanisms by which these sphingolipid signals, sphingosine and ceramide in particular, are able to modify the properties of cell membranes. The capacity of ceramide to catalyse the transbilayer (flip-flop) motion of polar lipids in membranes will be discussed, as well as the marked membrane-permeabilising effect of both ceramide and sphingosine. The behaviour of ceramide, glucosylceramide (cerebroside) and ceramide phosphorylcholine (sphingomyelin) in bilayers will be comparatively studied. Their effects on the lipid bilayer could be assimilated, respectively, to those of a wild tiger, a tamed tiger, and a caged tiger.

COLL 415

Correlation of an antimicrobial peptide’s potency and its influences on membrane elasticity

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The killing power of membrane-active antimicrobial peptides (AMPs) lies in their ability to disrupt the structures of pathogenic membranes. While understanding the AMPs’ mechanisms of action is key to realizing their therapeutic potentials, how the AMPs modulate membrane elasticity and thereby affect membrane structure remains an open question, even though the AMP-induced variations in membrane curvature are widely considered to be crucial. Here, we exploit the x-ray diffraction technique to examine how the dominant bacterial lipid, phosphatidylethanolamine, varies its monolayer elastic properties upon interacting with six artificial peptides mimicking the AMPs’ common
amino acid content. Remarkably, the monolayer spontaneous curvature $C_0$ is unaffected by any of the peptides. In contrast, the peptides designated as (K2W)$^2$, K4W2, R6, and R9, mimicking the AMP mutants with microbicidal potency, are able to modify the monolayer bending moduli $K_{cp}$, while those derived from the impotent mutants cannot. The results are consistent with the scenario that the AMPs disrupt the structure of pathogenic monolayers by, additionally if not exclusively, modulating their $K_{cp}$'s, with stiffening and softening leading to two different modes of disruption, that is, toroidal pore formation and membrane micellation, respectively.

**COLL 416**

**Quantifying the formation of functional colloidal nanoparticles through the understanding of surface chemistry**

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The ability to fine control the formation of nanoparticles in colloidal systems is a hallmark of modern synthetic nanotechnology. Understanding the interaction between additives (precursors and capping ligands) and growing surface of nanoparticles is essential to realize the promise of precision design of functional nanoparticles in colloidal systems. Recent developments of liquid-phase in situ techniques, such as liquid flow cell for transmission electron microscopy (TEM) and synchrotron-based X-ray analysis, have created both new opportunities and challenges in studying the colloidal nanostructures in reaction media in detail. The realization of effects of intermediates on the particle formation and the development of new formation kinetics are just two examples highlighting the progresses in the area. In this presentation, I will discuss the quantitative analysis of growth kinetics based on commonly used surfactants, such as oleic acid and oleylamine, and metal precursors including metal acetylacetonates. The focus will be on the development of analytical models based on the in situ experimental data using both the known Lifshitz-Slyosov-Wagner (LSW) theory and newly-developed coalescence kinetics.

**COLL 417**

**Manipulation of surface capping for controlled growth, transformation, and assembly of nanocrystals**

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Surface capping by ligands plays an important role in the controlled growth and transformation of colloidal nanocrystals. After many years of development, it has been widely accepted that capping ligands can affect the nucleation and growth behavior of nanocrystals during their solution phase synthesis. In this presentation, we show that the manipulation of surface capping offers more control over the behavior of
nanocrystals including their interactions, assembly, and chemical transformation. A special scenario of surface capping is when the amount of capping ligands is insufficient or the ligands only offer limited protection, the nanocrystals will self-assemble in order to gain higher stability, thus offer opportunities in controlling their secondary structures. As an example, we show that by controlling their density of surface ligands (and therefore surface charges), silver nanocrystals can be assembled into secondary structures with tunable plasmonic properties ranging from 400 nm to near IR. Moreover, the ligands on the nanocrystal surface confer highly reversible assembly and dynamic color change to the system as the surface charge can be conveniently manipulated. On the other hand, when nanocrystals are made to undergo chemical transformations, there are often accompanying, large mechanical deformations and changes to overall particle morphology. These effects can constrain the development of multi-step synthetic methods through loss of well-defined particle morphology and functionality. Here we also discuss surface protection may allow preservation of overall particle morphology despite large volume changes during their chemical transformation. The surface protected conversion strategy represents a general self-templating method for nanocrystal synthesis and can be applied to the chemical conversion of nanostructures of many morphologies (spheres, rods, cubes, and plates) and compositions (hydroxides, oxides, and metal-organic frameworks).

COLL 418

Single-crystal electrochemistry reveals why nanowires grow

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An increasing number of applications rely on metal nanowires grown in solution-phase syntheses, but the mechanism by which nanowires grow remains a matter of debate. Solution-phase synthesis generally involves heating a solution containing a metal salt, a reducing agent, and a shape-directing organic additive (usually referred to as a capping agent) that is necessary for anisotropic growth. Researchers have hypothesized that capping agents direct anisotropic growth of pentagonally-twinned Cu, Ag, and Au nanowires by selectively inhibiting atomic addition to the {100} facets on the sides of nanowires, leaving the {111} facets on nanowire ends open to atomic addition. This presentation will show how measurements with single-crystal electrodes can prove this hypothesis is false for two different syntheses of Cu nanowires. In one Cu nanowire synthesis, ethylenediamine acts as a facet-selective promoter of Cu nanowire growth by keeping the Cu(111) surface relatively free of surface oxidation in the highly basic growth solution (>12 M NaOH). This resulted in a ~6 minute window during which hydrazine reduced Cu ions onto Cu(111) while reducing surface oxides on Cu(100). The ~6-minute period of facet-selective Cu deposition closely matched the time scale over which Cu nanowires switch from longitudinal to lateral growth in the actual nanowire growth solution. In another synthesis in which hexadecylamine is thought to serve as a capping agent of {100} facets, electrochemical measurements show that
hexadecylamine does not selectively passivate Cu(100); it passivates both Cu(111) and Cu(100) equally. However, the introduction of Cl\textsuperscript{-} in a narrow range of concentrations selectively disrupts the alkylamine monolayer on Cu(111) and lowers the charge transfer resistance by 14.7 times relative to Cu(100). This narrow range of Cl\textsuperscript{-} concentrations exactly matched the concentration that produced Cu nanowires with the highest aspect ratio. Cu nanowires did not grow without Cl\textsuperscript{-}. DFT calculations corroborate synthetic and single-crystal results by showing that Cl\textsuperscript{-} can selectively displace hexadecylamine from Cu(111) but not Cu(100) at an intermediate monolayer coverage of 0.33. This second example illustrates how the combination of single-crystal electrochemistry and DFT can uncover the synergistic role halides and capping agents play in driving anisotropic growth.

**COLL 419**

**Temperature-dependent photoluminescence and stability of perovskite nanocrystal superlattices**

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The temperature-dependent photoluminescence (PL) spectra and lifetimes, and thermal stability of ordered assemblies, of methylammonium lead iodide (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}, MAPI) and CsPbX\textsubscript{3} (X=Cl, Br, I) nanocrystals were studied. These nanocrystals generally exhibit decreased PL lifetimes and decreased emission energy with lower temperature, unlike most semiconductors. Luminescent MAPI nanocrystals with cuboidal shape and tetragonal crystal structure are terminated by (110) and (002) facets based on grazing-incidence wide-angle scattering (GIWAXS) and high resolution transmission electron microscopy (TEM) and electron diffraction. *In situ* GIWAXS and GISAXS of the MAPI superlattices heated under nitrogen exhibit a phase transition from tetragonal-to-cubic structure at 60\textdegree C, similar to bulk MAPI. The MAPI nanocrystals start to decompose to PbI\textsubscript{2} at about 90\textdegree C, which is 10\textdegree C lower reported for bulk MAPI thin films, and at slightly higher temperatures, the coexistence of hexagonal and rhombohedral PbI\textsubscript{2} is observed. As PbI\textsubscript{2} precipitates, there is simultaneously fusion of the MAPI nanocrystals in the superlattice. The thermal stability of superlattices of \(\gamma\)-orthorhombic CsPbI\textsubscript{3} nanocrystals capped with either oleic acid (OA) or phosphinic acid (PA) were also studied. The capping ligands influences the orientation of the nanocrystals on the substrate, with OA and PA capping yielding nanocrystals oriented with (001\textsubscript{SL}) and (002\textsubscript{NC}) planes, or (110\textsubscript{NC}) and (002\textsubscript{NC}) planes, respectively, on the substrate. Heating the CsPbI\textsubscript{3} nanocrystal assemblies to 300\textdegree C induced a transition from the \(\gamma\)-orthorhombic to the \(\delta\)-orthorhombic (yellow phase) and the nanocrystals capped with PA were found to be more thermally stable than those capped with OA.

**COLL 420**

**Autocatalytic surface reduction and its role in the synthesis of metal nanocrystals**
Despite the universal role of autocatalytic surface reduction in the synthesis of colloidal nanocrystals, it is still poorly understood and controlled in terms of kinetics. Through the use of well-defined nanocrystals as seeds, including those with different types of facets, sizes, and internal twin structure, we have quantitatively analyzed the kinetics of autocatalytic surface reduction in an effort to control the evolution of nanocrystals into predictable shapes. Our kinetic measurements demonstrate that the activation energy barrier to autocatalytic surface reduction is highly dependent on both the type of facet and the presence of twin boundary, corresponding to distinctive growth patterns and products. Interestingly, the autocatalytic process is effective not only in eliminating homogeneous nucleation but also in activating and sustaining the growth of octahedral nanocrystals. This analysis represents a major step forward toward achieving a quantitative understanding and control of the autocatalytic process involved in the synthesis of colloidal metal nanocrystals.

**COLL 421**

**Importance of surface chemistry in synthesis, transformations, and sensing applications of plasmonic metal nanoparticles**

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Plasmonic metal nanoparticles (PMNPs), by virtue of their localized surface plasmon resonance (LSPR), are attractive for a range of applications centered in optics and sensing. Colloidally, PMNPs are largely limited to silver and gold nanoparticles. Silver is superior plasmonically and more amenable to shape-selective synthesis through oxidative etching, while gold features superior chemical stability – consequently, the composite Au-Ag PMNPs based on templating AgNPs can offer an optimal combination of functional properties. The surface chemistry of PMNPs is essential for their shape- and size-selective synthesis and transformations required for applications.

In the presentation, several topics based on our work with PMNPs will be reviewed from the perspective of nanoparticle surface chemistry: surface stability and species used in surface stabilization, modification and morphological control. First, synthesis of PMNPs will be considered in terms of two major pathways: thermal and photochemical, and their interplay with surface stabilization. Second, core-shell PMNP morphologies will be discussed, using an example of encapsulation of gold-plated silver PMNPs with metal oxide shells. The need for protective plating on AgPMNPs, the range of accessible metal oxides and conditions for uniform deposition with controlled shell thickness will be examined. Finally, surface plasmon resonance (SPR) sensing with PMNPs will be presented: sensing of surface-adsorbing species, the effect of morphological transformations, and approaches to impart sensing selectivity through the shell functionalities in core-shell PMNP morphologies.
COLL 422

Surface action spectroscopy: A new tool for the spectroscopy of surface vibrations

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Action spectroscopy with inert gas messenger atoms/molecules is commonly used for the characterization of clusters in the gas phase. With this method vibrational spectra of the clusters are measured via detection of inert gas desorption following excitation of cluster vibrational modes. We have constructed an apparatus for the application of action spectroscopy to surfaces of solids using light from the infrared free electron laser of the Fritz Haber Institute.

There are two channels leading to inert gas desorption in surface action spectroscopy. One channel is bulk sensitive and reflects the sample’s infrared absorption cross section. In this channel warming up processes induce inert gas desorption. The other, more interesting channel is surface sensitive – here energy of an excited surface vibrational mode breaks the bond between the inert gas messengers and the surface.
via vibrational coupling. This channel permits to get surface vibrational spectra without having to measure reference data as in the case of conventional infrared absorption spectroscopy. The sensitivity of the method depends on the messenger gas – the more weakly the atoms/molecules are bound, the more readily the bond may be broken by a vibrational excitation at the substrate surface. A relevant difference between infrared absorption spectroscopy and the surface action spectroscopy method is probably the possibility to selectively decorate surface features with messengers since in this case the signal comes only from the decorated surface features. Examples for the application of this method will be shown and discussed.

COLL 423

Extracting chemistry from the analysis of core-level spectra

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X-Ray Photo-electron Spectroscopy, XPS, is widely used to obtain information about both the composition and the chemical bonding of materials. The interpretation of the XPS in terms of chemical interactions is very commonly focussed on the shifts of core-level binding energies, BEs, to infer the chemical state of the material. In particular, a shift to higher BE is taken as indicating that the ionized atom is more positively charged, and the reverse is taken for shifts to lower BEs. However, there are other reasons for shifts in BEs besides charging; these include changes in hybridization and changes in bond distance. Furthermore, there are other features of the XPS besides BE shifts from which chemical properties of the material can be inferred. These include the number, width, and relative intensity of the main and satellite peaks of the often complex XPS spectra. The physical and chemical origins of these features allow them to be related, especially with guidance from theory, to the electronic structure of the material. An important mechanism is the angular momentum coupling of the open shell electrons which often leads to unresolved features and broad observed peaks. It will also be shown that this angular momentum coupling must be taken into account in order to understand the complex features observed in the near edge features of X-Ray adsorption. This subject is especially appropriate for a symposium honouring Prof. Hajo Freund since he has made pioneering contributions for the correct interpretation of XPS spectra.

COLL 424

Metal oxide – water interface: Quantum chemical studies compared to experiment

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The interaction of water molecules with oxide surfaces is studied for increasing loadings from isolated molecules to loadings beyond one monolayer. The oxides considered are SiO$_2$-bilayers supported on Mo, MgO(001), Al$_2$O$_3$(0001) Fe$_2$O$_3$(0001), Fe$_3$O$_4$(111). Issues addressed are the accuracy of the quantum chemical method applied, in particular of DFT+dispersion, the sampling of configurations for higher coverages, molecular vs. dissociative adsorption, and the identification of adsorption structures by comparison of observed and predicted vibrational spectra.

**COLL 425**

Composition and chemistry of liquid/vapor interfaces studied by liquid-jet x-ray photoelectron spectroscopy and molecular dynamics simulations

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We utilize ambient pressure x-ray photoelectron spectroscopy (APXPS) to probe the composition of the liquid/vapor interface of a solution micro-jet (25 micron diameter). The XPS spectra provide information on the composition and local chemical environment of the solution surface. Experiments carried out at synchrotron sources (ALS and BESSY II) allow us to vary the photon energy used in the XPS experiment—thus providing spectra over a range of photoelectron kinetic energies. Varying the photoelectron kinetic energy changes the “probe depth” of the experiment into the sample—thus providing information on the concentration profile of solutes into the solution. A variety of ionic and neutral solutes have been studied in water solutions. Highly miscible solutions (e.g. acetonitrile in water and ethanol in water) and less soluble solutes (e.g. organosulfur compounds—DMS, DMSO) have been studied. In all cases we observe surface segregation of the organic solute at low bulk concentrations. Details of the density profiles of a number of organic solutes in water will be presented along with MD simulations that provide insight into the solvation details that drive surface segregation in many systems. Recent experiments in which we utilize a two channel microfluidic mixing system to mix two solutions just prior to the formation of the free jet, and thus initiating a chemical reaction, will also be described.

**COLL 426**

Chemical dynamics in heterogeneous catalysis

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Model systems with well-defined atomic structures have created the experimental and theoretical basis of our understanding of catalysis. The evolutionary extrapolation to high-performance systems remains, however, illusive. This is commonly termed
“complexity” gap. The contribution shows how the multi-scale nature of kinetic interfacial processes induces additional novel chemical phenomena in reacting catalysts that do not occur in model systems and remain thus uncovered in our rigorous understanding. The concept of frustrated phase transitions for performance systems relates the combined effects of elevated chemical potentials to the function of catalytic materials.

**COLL 427**

**Structuring of organic solvents at biointerfaces and its ramifications for antimalarial inhibition of hematin crystallization**

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Hematin is a byproduct of heme detoxification in malaria parasites. Current antimalarial compounds have been shown to inhibit the growth of hematin crystals, referred to as hemozoin (*in vivo*) or b-hematin (*in vitro*). Identification of antimalarial drug action on this phase transformation could provide a foundation for drug design to overcome parasite resistance to antimalarials. Continued resurgence of antimalarial drug resistance drives research efforts to better characterize drug-crystal interactions from a fundamental perspective. To this end, we aim to better understand the molecular mechanism(s) of hematin crystallization and antimalarial drug action within physiologically-relevant environments as the basis for elucidating growth sites on hematin crystal surfaces and design more effective growth inhibitors that selectively bind to these sites.

We employ *in situ* atomic force microscopy (AFM) in parallel with bulk crystallization studies and molecular modeling as a platform to study the mechanisms of crystal growth and inhibitor-crystal interactions in biomimetic growth solutions. Time-resolved *in situ* AFM measurements reveal that hematin crystallization occurs by single molecule incorporation, specifically involving two-dimensional nucleation of layers. We have quantified the rate of layer generation and the velocities of anisotropic step advancement as a function of supersaturation in the absence and presence of antimalarials, from which we identified unique modes of binding for current antimalarials as inhibition pathways. Moreover, we have shown that crystal growth occurs in a complex medium comprised of organics (neutral lipids) and water. In this talk, we will show how a biomimetic growth mixture comprised of n-octanol (lipid surrogate) exhibits unique binding modes at solid interfaces, which can alter the adsorption of antimalarials. Collectively, our findings reveal fundamental principles governing the molecular recognition of antimalarial drugs to specific sites that could lead to the rational design of new compounds with improved efficiency to overcome parasite resistance to current antimalarials.

**COLL 428**
Real-time chemical imaging of carbon-dot-templated tubulin-polymerization

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The effect of microtubule (MT) polymerization in presence of Carbon Dots (CDs) has not been heavily explored. To understand their role in the MT polymerization we report the polymerization kinetics analyzed with Infrared (IR) spectroscopy and imaging of tubulin in the absence and presence of select CDs. Our analysis not only complement the kinetics information measured with fluorescence for the tubulin system but also provide valuable information regarding the MT structural evolution and its spread within the structure. While our biochemical investigation point to the propensity of a certain monomer to polymerize, IR spectroscopic imaging studies in a microfluidic device reveal a distribution of completely different secondary structures (more pronounced $\beta$-sheets) for a CD mediated polymerization as opposed to an uninhibited case. We attribute the variation in the kinetics to arise from the difference in the number of $-\text{CH}_2$and $-\text{NH}$ bond formation on polymerization. However, we argue, the overall polymerization kinetics is dictated by the formation of $\alpha$-helical structures for both uninhibited and CDs regulated cases. Infrared images of dried MTs generated from tubulin incubated CDs reveal its spectra characteristics all over the structure, which prompts us to infer about CDs serving as a serving a template for MT polymerization.

COLL 429

Catechin-mediated restructuring of a bacterial toxin inhibits activity

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It has been reported that catechins have antibacterial, anti-toxin, and membrane-altering properties. For example, catechins have been demonstrated to inhibit the activity of the leukotoxin (LtxA) produced by Aggregatibacter actinomycetemcomitans, although the mechanism of this inhibition was unknown. We hypothesized that catechin-mediated changes in membrane properties inhibit bacterial toxin binding, thus leading to the reported anti-toxin properties. To test this hypothesis, six common catechins were used: (--)-catechin (C), (--)-epicatechin (EC), (--)-epigallocatechin (EGC), (--)-gallocatechin gallate (GGC), (--)-epigallocatechin gallate (EGCg) and (--)-epicatechin gallate (ECg) to correlate inhibition of LtxA activity with the catechins’ ability to alter the host membrane properties. Our results indicate that the catechin-mediated decrease in host cell membrane fluidity does not contribute to the reported anti-toxin mechanism of catechins. Even more, pre-incubation of LtxA with catechins is more effective in the prevention of cytotoxicity than pre-incubation of cells with catechins, suggesting that the catechins act on the toxin rather than the cell membrane to inhibit LtxA activity. Consistent with this finding, we found that the catechins decreased the affinity of LtxA
for cholesterol, an interaction required for cytotoxicity. In each of these experiments, GCg, EGCg, and ECg were more effective than C, EC, and EGC. Binding of LtxA to cholesterol is mediated by a cholesterol-binding motif located in the C-terminal end of LtxA; we, therefore, suspected that catechins might alter the exposure of this domain by altering the toxin’s secondary structure. Using circular dichroism spectroscopy, we found that the secondary structure of LtxA is drastically changed when the toxin is treated with EGCg, but not with C, suggesting that galloylated catechins modify protein toxin structure, thus inhibiting the toxin from binding to the host cell surface.

Coll 430

Molecular dynamics simulation study of the effect of lignin dimers on the gel to liquid-crystalline transition temperature in DPPC bilayers

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Interactions between DPPC lipid bilayers and lignin G-G dimers (coniferyl alcohol) and their derivatives were studied using molecular dynamics (MD) simulations. Commercial G-G derivatives (CGds) and benzene modified G-G dimers (BMGds) show a higher affinity for the bilayer interior than natural dimers. In this study we compare MD results for the gel to liquid-crystalline transition temperature (Tm) with differential scanning calorimetry (DSC) experiment results. Specifically, the MD simulation systems studied consist of fully hydrated DPPC lipid
bilayers in the presence of different concentrations of lignin dimers. After initial equilibration of the systems a cooling followed by a heating procedure is used to take the lipid bilayer from a liquid-like state to a gel-like state and then back. We captured the transition from gel to liquid phase by defining and analyzing of a normalized deuterium order parameter (NScd) averaged over all carbon atoms located in the middle of the lipid tails. Typically, with varying temperature the NScd exhibits, well defined, slightly different slopes at the beginning and at the end of the temperature interval and a relatively large slope change in the intermediate range, around the transition temperature $T_m$. The MD results show a very sharp and clear drop for a pure DPPC bilayer with $T_m$ of 316.5 K which is very close to the experimental value of 314 K. However, once lignols are added to the system, the signal becomes nosier and wider. For 20 mol % lignols/lipids of CGds and BMGds, $T_m$ shifts by -7.1K and -6.7K, respectively. This is qualitatively consistent with experimental values of -1.5K and -6 K. For 40 mol% lignols/lipids of CGds and BMGds, $T_m$ shifts by -25K and -24.3K, respectively. While the trend for 40% is still correct, the MD shifts are much larger than from DSC. We further analyze the MD trajectories and study the location of the lignols and their effects on bilayer structure to explain the observed trends.

**COLL 431**

**Multiscaling method for systematic investigation of nanostructure-biointerface interactions in crowded biological media**

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Molecular interpretation of experimental data in complex fluids often requires simulations of systems at high concentrations or in states of moderate-to-high local crowding. These include data from both established and emerging technologies, including imagining, microfluidics, surface plasmon resonance, and biosensors. Of increasing interest is the design of functionalized nanostructures for applications in nanomedicine, including diagnostics and therapeutics. A method is presented for the systematic investigation of such systems through computer simulations. The roots of the method were recent needs to explain the behavior of ultrasmall nanoparticles in blood serum, as measured with DLS; to understand the size-dependent aggregative behavior of gold nanoparticles in biofluids, as measured with AUC; and to explain dramatic changes in protein-nanoparticle binding kinetics upon seemingly modest changes in surface chemistry, as inferred from SPR experiments. The method described here embeds unique features that makes it a valuable tool for the design of novel experiments and to provide molecular interpretation of experimental data. Applications is illustrated through the design of nanostructures of various shapes (e.g., spheres, plates, rings, tubes, and rods), crystal compositions (with emphasis on magnetite and gold), and surface chemistries; the effects of these design parameters on the interactions with biologically active proteins and lipid membranes will be discussed.

**COLL 432**
Functionalization of cotton fabric substrate for enhanced sequestration of Doxorubicin (DOX) chemotherapeutic agent

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The most common treatment of hepatocellular carcinoma is chemotherapy via transarterial chemoembolization (TACE) using doxorubicin (DOX) chemotherapeutic agent. DOX preferentially binds to guanine-cytosine sites in DNA and inhibits replication. TACE allows a significant amount of DOX dosage to be administered directly into the tumor to reduce its size by destroying the rapidly dividing cells, however, the remaining drug enters systemic circulation where it also destroys healthy cells. To prevent DOX systemic circulation and reduce side effects, this research seeks to develop a filter device that will be deployed downstream from the tumor to capture residual DOX, isolating its presence in the hepatic tumor. Cotton fabric was used as a substrate to assess DOX sequestration capability then coated with functionalized with silanes which served as DNA linking molecules. 3-glycidoxylpropyltrimethoxy silane (GDPTMS), 3-isocyanotopropyltrimethoxy silane (ICPTMS), and 3-aminopropyltriethoxy silane (APTES) were applied to the surface via chemical vapor deposition (CVD) and via reaction in toluene. Herring DNA was reacted with surface functional groups and the reaction confirmed via Energy-dispersive spectroscopy (EDS). The functionalized cotton was then immersed in DOX solution at physiological temperature to assess capture capability with increasing time. Fluorescence spectroscopy determined the ICPTMS-coated sample showed the most DOX capture after 1 minute (17%) and after 10 minutes, both ICPTMS and APTES-coated samples captured 66% of DOX present in solution. The capability of the functionalized cotton surfaces to sequester DOX in complex media will be assessed in phosphate buffer solution (PBS) and blood serum. Additionally, various silanes will be used to enhance reactivity with DNA and increase DOX capture.

COLL 433

Blood filtration: Materials to modulate systemic immune responses

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Materials to control immune responses can mitigate the systemic inflammatory response syndrome (SIRS) during life-threatening inflammatory conditions such as sepsis. Our research focuses on the synthesis of protein-polymer conjugates on surfaces to remove deleterious cytokines from circulating blood to improve sepsis survival rates.

Sepsis remains the most common cause of death for intensive care unit (ICU) patients with a 25-50% mortality rate. Fatalities from severe sepsis is due to SIRS, which is manifested by a cytokine storm. The imbalance of specific inflammatory and anti-
inflammatory cytokines during SIRS may lead to organ failure and death. To modulate the cytokine storm, specific cytokines must be removed at precise times. To this end, we modified the surface of blood bioreactors with humanized antibodies to remove specific cytokines with temporal control. To increase filtration efficiency while further minimizing non-specific protein binding, we are now developing low-fouling bimodal poly(carboxybetaine) surfaces for antibody immobilization using surface initiated (SI) RAFT polymerization. To date, two-layer, bimodal surface architectures have been developed for SI-ATRP and SI-PIMP. These architectures employ a short dense anti-fouling brush layer and a sparse, thick layer for improved bioconjugation density, providing increased separation and sensing capacity. We developed a method of multi-modal RAFT polymerization to produce tunable mixtures of well-defined poly(carboxybetaine) in solution as well as on silicon surfaces, via the partial termination of macro-CTAs. SI-RAFT polymerization is well suited to these biomedical applications as it does not require any transition metals in synthesis.

**COLL 434**

**Homogeneous immunoassay for the detection of EGFR-HER2 heterodimerization on cell surfaces**

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Disrupting pathogenic protein-protein interactions (PPIs) is an effective targeting strategy in cancer treatment. The homo- and heterodimerizations of the HER family receptors are particularly important, with the approved drug Perjeta® (Pertuzumab) inhibiting dimerization. Although there are many techniques used to evaluate and discover PPIs inhibitors, those techniques often require fusing or conjugating a reporting probe to the proteins involved in PPIs - this is concerning as changing the structures of proteins can alter their native behavior. We have developed a rapid assay to monitor the PPI of EGFR-HER2 dimerization without interference. Our assay, called Target Engaged Complementation (TEC), utilizes a three-part split version of the NanoLuc® (Promega) luciferase where two peptide fragments of the luciferase (b9 and b10) are each fused to antibodies binding to EGFR and HER2. As EGFR and HER2 dimerize, the antibody fusions come in proximity, bringing the two small fragments together. When the third part of the luciferase (d11S) is added, all three pieces re-fold into full luciferase producing a glow-type luminescent signal. The luminescence directly correlates to the level of EGFR-HER2 dimerization increase, making it a facile measurement of this important PPI. We demonstrate successful detection of EGFR-HER2 dimerization on cells that express both EGFR and HER2. We confirm that TEC is sensitive and can differentiate dimerization levels induced by various concentrations of EGF and different levels of EGFR and HER2. Importantly, we can monitor both induction and disruption of the dimerization. Monitoring pathological PPIs can guide effective disease targeting strategies and identify novel PPI inhibitors.
Nanoparticle technology has been a growing field in biomedical research. This is in part due to potential applications in drug delivery, biosensing, diagnostics, and imaging. We must perceive the interaction of nanoparticle with biomolecules, in order to integrate those into biological systems. Understanding of such interactions, structure, and dynamics of biomolecules on nanoparticles are highly desired. Solution NMR can be used as a novel method of identifying characteristics of biomolecules when they interact with nanoparticles. Our previous work suggests that GB3 protein makes a monolayer on gold nanoparticle (AuNP) surface and remain globular. We have employed hydrogen-deuterium exchange (HDX) to determine the tertiary structure of GB3 on AuNP surface.
Remarkably the same residues were protected in both AuNP surface-bound and GB3 in solution and correlate with each other. The HDX rates of the AuNP surface-bound protein was notably lower than the free protein in solution. These results suggested that the binding with AuNP surface increase the protection of residues against D2O and surface-bound GB3 retains its native structure. The orientation of GB3 was determined by carrying out two novel experiments; competitive binding and methyl labeling of lysine residues. To perform competitive binding experiments we have mutated all the lysine residues to alanine one at a time and competed GB3 variants with WT GB3 in the same solution with AuNP to observe how the binding capacities vary with wild-type GB3. Notably the binding capacity ratio was lower for three lysine residues; namely K4A, K13A, and K50A which were identified from our previous work as well. Methyl labeling of lysine residues confirmed the β-sheet region oriented towards AuNP surface which we identified from competitive binding. We have carried out same methylation experiments for immunoglobulin G (IgG) and Serum Albumin to observe that surface lysine residues are responsible for attachment with AuNP surface. The results reported here have profound significance in identifying protein structure and orientation on the AuNP surface.

COLL 436

Reducing protein adsorption on biomimetic superhydrophobic surfaces: Hybrid hydrophilic-hydrophobic arrays prepared by 3D printing

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Superhydrophobic (SH) surfaces have been explored for various applications in microfluidics, immunoassays, cell and tissue manipulations, and biosensors due to their excellent liquid repellency, easy droplet manipulation, self-cleaning and low adhesion properties. Naturally occurring SH surfaces (e.g. lotus leaves, cicada wings, and water strider legs) inspired scientists to prepare biomimetic super repellent surfaces using various synthetic materials. Due to the reduced solid-liquid contact area, SH surfaces have the potential to reduce the amount of protein adsorbed over an area. Thus they could improve the signal to noise ratio and accuracy of most immunoassays, which are otherwise limited by non-specific protein adsorption.

Here, we present a simple method to fabricate hybrid SH surfaces through introduction of overhangs/re-entrant structures from a combination of hydrophobic and hydrophilic materials using 3D-printing. The effect of surface roughness and chemistry on protein adsorption was studied using confocal fluorescence microscopy (CFM) and roll-off angle measurements. The location and movement of the solid-liquid-vapor triple contact line into the plastron was observed in-situ using a fluorescently labelled BSA protein
solution. These surfaces maintain stable superhydrophobic properties even when challenged with protein solutions for over 2 h. This stability of superhydrophobic properties promises to be useful for manipulation of aqueous protein micro-droplets and solutions for biomedical applications.

COLL 437

Gold nanoparticle imaging in complex mammalian cell cultures

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Gold nanoparticles have found many uses in biomedicine, opening doors in imaging modalities, hyperthermia, and drug delivery, among others. The high degree of control over their physical properties and their surface functionalization allows one to produce a library of nanoparticles for labelling purposes, taking advantage of their plasmonic and Raman signal-enhancing effects for local heating and Raman-microscopy respectively. We are interested in the use of such nanoparticles to label both biological and non-biological 3D structures, printed using 3D printing or produced with bottom-up methods. This includes a wide range of systems such as the growth of living cells in defined morphologies due to their natural predisposition (layered or spherical forms), 3D printing of living cells embedded in biological gels, 3D printing of nanoparticle containing inks etc. Our goal is to be able to use the defined nanoparticles as combined sensors and “GPS” tags, thereby giving biological information with a precise localisation in a complex 3D system.

We have focused on gold nanostars and nanorods as two different nanostructures with highly defined plasmonic properties, both of which can be also surface functionalised to have opposing surface charges. Additional nanostructures and material composition can also be used to increase the library of nanoparticles (for examples nanospheres, incorporation of iron oxide nanoparticles or silver doping, etc). As for the cellular system, we have used cell combinations which aim to recreate aspects of the \textit{in vivo} environment, such as heterotypic cell mixtures or 3D cell growth. The results presented will aim to highlight the flexibility of such nanoparticles for multimodal 3D imaging and sensing.

COLL 438

Live-cell encoding by single-nanoparticle FRET multiplexing

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Optical encoding based on nanoparticles provides many advantages for multiparameter imaging. Encoding based on quantum dots (QDs) attracted considerable attention due to their unique optical properties. However, most approaches apply mixing QDs of
several colors or lifetimes in different proportions. Designing different concentration-independent codes without mixing various nanoparticles and by using single-wavelength excitation and emission for multiplexed imaging is extremely challenging. Here, we report the synthesis of QDs coated with SiO$_2$ of different shell thicknesses (6 and 12 nm). Attachment of lanthanide (Ln) complexes (Tb and Eu) with long photoluminescence (PL) lifetimes on the SiO$_2$ shells resulted in different Ln-to-QD distances, which, in turn, led to different PL decay times due to distance-dependent FRET. Thus, four specific QD PL decays (all at 640 nm upon excitation of the Ln complexes at 349 nm) were designed with Tb-QD(SiO$_2$-6nm), Tb-QD(SiO$_2$-12nm), Eu-QD(SiO$_2$-6nm), and Eu-QD(SiO$_2$-12nm) and used as well-defined single-particle codes to label living cells. To recognize the live-cell codes, time-gated fluorescence microscopy was employed and four different cell types could be distinguished by a single measurement. The information density of the single particle encoding can be further enlarged by using donors with various Ln complexes and QD acceptors with different colors. Thus, our time-gated Ln-to-QD FRET concept has the potential to significantly advance fluorescence cell-encoding.

Figure 1. (a) QDs with SiO$_2$ coatings of different thicknesses ($x=6$ or 12 nm) functionalized with Eu-1 or Lumi4-Tb for single-wavelength temporal PL barcoding. (b) The RGB encoding principle based on three distinct TG PL intensity fractions for each of the four FRET-specific PL decays and four encoded cells.

COLL 439

Unraveling the origin of plasmon-coupled circular dichroism from gold nanorod-protein complexes at single-particle level

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Plasmon-coupled circular dichroism (PCCD) has emerged as an intriguing technique for sensitive detection of biomolecules through strong coupling between molecular chirality and plasmon. However, PCCD observed with ensemble spectroscopy in plasmonic colloids are always biased without considering the presence of some aggregation. Plasmonic aggregates themselves could be chiral, which has been demonstrated by many reports including our extensive single particle work. However, none of this (chiral aggregates) has been considered so far because of the origin of PCCD really not distinguishable with ensemble methods. In this talk, I will discuss our recent work on applying single particle measurements for the first time and can distinguish the different contributions between structural chirality of aggregated nanorods and PCCD induced from chiral proteins. I will also discuss how this work sheds light on designing a better single-particle plasmonic platform for detecting biomolecules at single-molecule level.

COLL 440

Engineering nanomaterials for imaging and therapy of bacteria and biofilm-associated infections

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Infections caused by multidrug-resistant (MDR) bacteria pose a serious global burden of mortality, causing thousands of deaths each year. The “superbug” risk is further exacerbated by chronic infections generated from antibiotic-resistant biofilms that are highly resistant to available treatments. Here, we report surface-engineered nanomaterials as potent imaging and therapeutic agents for bacterial infections. Systematic investigation of antimicrobial activity of oxanorbornene-polymer derivatives generated polymer nanoparticles with unprecedented therapeutic selectivity towards MDR bacteria (5-fold higher selectivity than previously reported studies). Additionally, polymeric nanoparticles prevented onset of resistance development in bacteria for ~1300 generations and eradicate biofilms on infected mammalian cells, a feat unachieved by previous antimicrobial polymers. In further study, surface monolayer of hydrophobic ligands facilitated our nanoparticles to block bacterial efflux pumps, yielding 16-fold reduction in antibiotic dosage to treat pathogenic bacteria including methicillin-resistant S. aureus (MRSA). Whereas, functionalization of nanoparticle surface with pH-responsive ligand enabled us to develop a general strategy to target and image bacterial biofilms for a broad-range of species. Subsequently, we utilized engineered polymers to generate nanosponges through self-assembly of polymers around essential-oil based cores for topical treatment of wound biofilms. Overall, our results show strong potential as an infectious disease therapeutic while simultaneously
provide a rational approach to design novel antimicrobials for sustainably combating bacterial infections.

Diagram showing polymeric nanoparticles to treat bacteria/biofilms while maintaining fibroblast viability and delaying the onset of resistance in MDR bacteria.

**COLL 441**

**Magnetic iron oxide nanoparticles grafted with a thermosensitive polypeptide brush: Uptake by tumor cells and cytotoxicity upon magnetic hyperthermia**

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Magnetic hyperthermia (MH) is envisioned to become a powerful therapeutic method by oncologists to fight against incurable cancers such as glioblastoma. Development of appropriate biocompatible coatings is critical for clinical translation of MH-agents. With this aim, we have synthesized and studied, *in vitro* and *in vivo*, superparamagnetic iron oxide nanoparticles (IONPs) coated with thermosensitive recombinant elastin-like polypeptides (ELPs). Magnetic IONPs were synthesized by a polyol pathway with either monocore (nanospheres) or multi-core (nanoflowers) morphology, low size-dispersity
and suitable heating efficiency under an alternating magnetic field (AMF). These were functionalized through strong coordination bonding of a phosphonate-terminated diblock ELPs. Large temperature variations of the sample were obtained in few minutes by applying an AMF and fast size changes of γ-Fe₂O₃@ELP nanoparticles were measured by in situ dynamic light back-scattering. Cellular internalization and toxicity assays were performed on a glioblastoma human cancer cell line. Superior cellular uptake was observed for multicore IONPs as compared to monocore IONPs, as well as for IONPs@ELP as compared to IONPs@PEG controls prepared from the same (spherical) cores. The internalization pathway in lysosomes was monitored by electron microscopy on microtomes and confocal optical microscopy on live cells. Cellular toxicity after AMF application with these core-shell IONPs was ascribed to lysosomal membrane rupture and leakage into the cytosol. Equal sharing of the magnetically loaded lysosomes among daughter cells during cell division suggest the possibility of successive application of MH on time scales superior to the cellular life cycle. Preliminary in vivo experiments evidenced the positive effect of the ELP brush as compared to the PEG brush used as control on γ-Fe₂O₃ nanoparticles biodistribution.

COLL 442

How the toxicity of nanomaterials towards different species could be simultaneously evaluated: A multi-nano-read-across approach

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The present study is aimed to develop a multi-nano-read-across modeling technique that helps in predicting the toxicity of different species such as bacteria, algae, protozoa, and mammalian cell lines simultaneously. Herein, the experimental toxicity of 184 metal and silica oxide (30 unique chemical types) nanoparticles from 15 datasets is analyzed. A hybrid quantitative multi-nano-read-across approach that combines interspecies correlation analysis and self-organizing map analysis is developed. In the first step, hidden patterns of toxicity among nanoparticles are identified using a combination of methods. Subsequently, the developed model based on categorization of the toxicity of the metal oxide nanoparticle outcomes is evaluated via the combination of supervised and unsupervised machine learning techniques to determine the underlying factors responsible for the toxicity.
Real-time monitoring of “soft” and “hard” protein corona in carbon dots via a microfluidic setup

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When nanoparticles (NPs) enter a biological fluid (such as human plasma), proteins, lipids, and other biomolecules adsorb on the nanoscale surface consequently leading to the evolution of a protein shell, famously referred as protein “corona”. The corona formed is dynamic in nature and changes over the due course of time owing to a combination of protein association and dissociations events. Furthermore, the composition of the corona is highly dependent on the surface chemistries of the NPs which dictate whether a ‘soft corona’ or a ‘hard corona’ gets formed, thereby ultimately affecting its biological response. Hence, understanding of the dynamic formation of protein corona process is a critical and important step in understanding the relationship between surface chemistry of NPs and its biological outcomes. In this work, we use a microfluidic platform to monitor the formation of a biomolecular corona of NPs having
different surface headgroups in a time-resolved manner. A distinct advantage of using such a setup over conventional in-situ measurements is a creation of a dynamic environment with accurate control over fluid flow allowing shear force being imposed on NPs and proteins resulting in their rigorous mixing thereby simulating a realistic biological milieu. We successfully demonstrated that NPs with cationic head-groups form a hard corona whereas NPs with neutral and zwitterionic surface groups formed a weak corona owing to their low non-fouling properties. We further analyzed the corona and its composition using different techniques such as dynamic light scattering, zeta potential, excitation-emission profiles, 1D SDS-PAGE and subsequently, LC-MS analysis. Ultimately, controlling the adsorption of proteins on NPs by tailoring the chemical motifs at its surface in a dynamic setup would be a valuable tool with promising therapeutic benefits in drug delivery and targeted cancer treatment.

COLL 444

Deciphering uptake and trafficking of nanostructured materials built from immune signals

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Initiating an immune response requires specialized antigen presenting cells (APCs) to present foreign antigens with co-stimulatory molecules. Toll-like receptors (TLRs) are often involved in expression of co-stimulatory molecules. TLRs detect patterns common in viruses and bacteria, but not humans. Both the location and frequency of TLR agonist (TLRa) detection help define the type of immune response generated. Simple platforms allowing control over how and where immune signals are processed would improve rational vaccine design. Using electrostatic interactions, we synthesized immune polyelectrolyte multilayers (iPEMs) composed entirely of anionic TLRa and cationic peptide antigen. This approach confers advantages of biomaterials (e.g. co-delivery) without carrier components. This simplicity allows isolation and quantification of synergies achieved by packaging immune signals into particles. We hypothesized co-delivery of TLRa and antigen in iPEMs would enhance immunogenicity over soluble delivery. iPEMs were incubated with primary APCs to study particle-cell interactions over time. iPEM treatment promoted co-internalization of both antigen and TLRa (A) through caveolae-mediated endocytosis (B). Uptake of iPEMs by APCs began in minutes (C), and drove faster downstream processing and APC activation relative to dose-matched free TLRa (D). Our findings provide insight into specific mechanisms by which particulate vaccines enhance initiation of immune response; insight that can be used to design vaccines with precise control over immune response.
A) iPEM treatment of APCs leads to co-delivery of antigen and TLRa (antigen+TLRa+). B) APCs treated with total inhibitor of endocytosis (2-deoxy-D-glucose, 2DG) or inhibitor of caveolae-mediated endocytosis (Filipin) revealed iPEMs are internalized in part by caveolae-mediated endocytosis. C) APCs incubated with iPEMs revealed an increase in the number of iPEMs/cell over time leading to more efficient APC activation compared to dose-matched soluble TLRa (D).

**COLL 445**

**Understanding the effects of surface coating and nanocrystal shape on corona formation for gold colloids**

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It is accepted that protein corona formation on colloidal nanomaterials is mostly promoted by nonspecific adsorption of serum proteins on poorly controlled nanoparticle surfaces. This issue has attracted considerable interest over the past decade, due to its detrimental impacts on the potential application of these materials in nanomedicine. However, most studies were carried out with a focus on spherical nanocrystals. Herein, we investigate the effects of combining the surface coating structure and charge with the nanocrystal shape on the corona formation using spherical, rod-like, and star-shape gold nanocolloids. The surface coating relied on lipoic acid-modified polymer ligands. We find that in the absence of PEG blocks in the surface coating, protein adsorption can be strongly affected by the exact structure and shape of the colloid. As such, corona formation substantially varied between spheres, rods and stars. These effects persisted under different incubation temperatures. In contrast, we find that introduction of PEG blocks or zwitterion moieties tend to drastically reduce nonspecific interactions and corona formation on all shapes of nanocrystals.

COLL 446

Carrier dynamics in plasmonic nanostructures

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Aluminum nanostructures support tunable surface plasmon resonances and have become an alternative to gold nanoparticles. While gold is the most-studied plasmonic material, aluminum has the advantage of high earth abundance and hence low cost. In addition to understanding the size and shape tunability of the plasmon resonance, the fundamental relaxation processes after photo-excitation must be understood to take full advantage of aluminum nanostructures in various applications including photocatalysis and photodetection. In this work, we investigate the energy relaxation after ultrafast pulsed excitation and the launching of acoustic vibrations in individual aluminum nanodisks with varying diameters using single-particle transient extinction spectroscopy. We compare the results to individual and coupled gold nanostructures that are studied through a combination of various single particle techniques: pump-probe transient extinction spectroscopy, photothermal imaging, and emission spectroscopy.

COLL 447

How adsorbates influence plasmon dephasing and relationships to photocatalysis

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Recently, evidence has been reported in literature that catalytic reactions can be facilitated on the surface of coinage metal nanoparticles through the excitation of localized surface plasmon resonances. Measurements made using low intensity continuous wave sources to excite plasmon-mediated catalysis, in addition to wavelength and isotope dependent photocatalytic rate measurements, suggest that plasmons facilitate catalytic reactions through non-thermal processes. However, details of how the energy stored in surface plasmons flows into the promotion of bond-making and bond-breaking steps are not known. A prevailing theory is that plasmons dephase through Landau damping to form “hot” electrons and holes in the metal and subsequently, hot carriers transport to the adsorbate-metal interface and transiently localize in adsorbate resonance states, thereby depositing energy into potential energy surfaces as described in the original Menzel Gomer Redhead model. Another possibility is that adsorbate resonance states act as scatterers that induce the dephasing of plasmons, thereby directly populating adsorbate resonances in localized electron-hole pairs across the metal-adsorbate interface – this process is known as chemical interface damping (CID). Here we will discuss experimental evidence suggesting that the second mechanism is most likely responsible for plasmon-facilitated catalytic processes on metal nanoparticle surfaces.

**COLL 448**

**Gold nanorods: SAXS studies of their growth and the effects of hydrostatic pressure**

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In this talk I will present results of in situ studies on the growth of gold nanorods using combined synchrotron SAXS measurements combined with spectroscopic measurements of the spectra of the growing crystals. We can directly measure the length and width of the rods using SAXS as a function of time, allowing symmetry breaking to be observed. We find there are two key changes in growth dynamics with an early breaking of spherical morphology and a subsequent "explosive" growth of the rods. We show how these critical points in the crystal growth are affected by gold ion concentration, reductant concentration and pH.

In the second part of the talk, I will discuss how hydrostatic pressure affects the spectrum of gold nanocrystals, both spheres and rods. Pressure affects the surface plasmon resonance and also the refractive index of the medium. We extract the bulk modulus of the gold particles and obtain a value of 190GPa, significantly higher than the bulk value of 167GPa.

**COLL 449**

**Gold nanorods with ultranarrow LSPR bands**
Although seeded-growth methods have made available to us an extensive library of anisotropic metal nanoparticles, the chemical complexity of the growth solution, often involving organic additives, and the structural instability of the seeds hinder the quest for high quality products. For the sake of synthetic simplicity, merging different synthetic protocols by finding common growth routes, is a mandatory step to reach a universal growth mechanism and reproducible fabrication. This communication will introduce two recent discoveries, related to improving the optical quality of both pentatwinned and single crystal gold nanorods.

We recently demonstrated that a thermal treatment of small seeds results in extensive twinning and a subsequent drastic yield improvement (>85%) in the formation of different types of pentatwinned nanoparticles, including nanorods, with a high monodispersity and tunable aspect ratio. On the other hand, although single crystal Au nanorods can be readily obtained with very high quality directly from optimized seeded growth methods, polydispersions below 10% are still difficult to reach, which leads to some broadening of the longitudinal LSPR band. We show here that femtosecond laser irradiation may lead to significant narrowing of the LSPR band, even to the limit of the single particle, as calculated from theoretical models, meaning pure "optical monodispersity".

**COLL 450**

**Next-generation anisotropic and optical materials: Imaging**

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Quantitative imaging of organic molecules that decorate the surfaces of inorganic nanomaterials is challenging. Here we report results of STEM/EELS experiments in which ligand density can be quantified on gold nanorods, as a function of position around the rod. Making this possible is a new technique to allow aqueous-based nanoparticles to be deposited on single-layer graphene substrates without substrate rupture.

**COLL 451**

**Cancer diagnosis and response to treatment with plasmonic nanoprobes**

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In the past two decades, plasmonic nanostructures have gained tremendous interest as both diagnostic and therapeutic agents for cancer detection and treatment. In this talk I will show the utility of gold nanostar probes designed in my lab for rapid and noninvasive detection of multiple immunomarkers of cancer to enable patient selection for immunotherapies, as well as response to treatment after immunotherapy. We combined a clinical and pre-clinical imaging technique, positron emission tomography with surface-enhanced Raman spectroscopy (ImmunoPET-SERS) in vivo by labeling gold nanostars with radiolabels, Raman reporter molecules, and targeting antibodies. Multimodal ImmunoPET-SERS seamlessly integrates depth-resolved whole-body imaging and high sensitivity of PET with high spatiotemporal resolution and multiplexing of SERS providing dynamic immunomarker profiling in vivo. Further, ImmunoPET-SERS was used to determine the immunomarker status of mice treated with combinatorial immunotherapy; we demonstrated real-time feedback of CD8+ infiltration in tumors which was confirmed with IHC ex vivo. High resolution SERS maps of tumor sections provide quantitative measure of multiple receptor expression in the same tumor section which correlate well with histological analysis of tissue.

COLL 452

Protein adsorption on inorganic nanoparticles in complex environments

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Proteins adsorb on the surface of inorganic nanoparticles and such form an "organic" coat. This process can be followed by measuring changes in effective size of the nanoparticles. This is for example possible by measuring diffusion processes of nanoparticle-protein complexes. Different methods to perform such measurements will be discussed and possibilities to perform such analysis in complex environments will be outlined.

COLL 453

Integrating nanoparticles and transition metal catalysts for bioorthogonal chemistry: Imaging and therapeutics using engineered nanoparticle ‘nanozymes’

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We are developing nanoparticle catalysts whose structure and function mimic those of enzymes. These ‘nanozymes’ use hydrophobic monolayers on gold nanoparticles to encapsulate transition metal catalysts (TMCs), The monolayer both protects the TMC and controls access to the ‘TMC ‘active site’. In our research we are employing these nanozymes to perform bioorthogonal chemistry in living systems, providing access to new modalities for biomedical applications. The use of these systems as therapeutic
and imaging agents for mammalian cells and bacterial biofilms (Figure 1) will be discussed.

Figure 1. Nanozyme-mediated imaging of bacterial biofilm (red) in a bacteria-fibroblast coculture.

COLL 454

Tailor-made surface modifications of nanocrystals for applications in materials and life sciences

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Almost all applications of nanocrystals require the control of surface properties in respect of solubility, miscibility, biocompatibility, passivation of surface states as well as electronic and magnetic interaction with the environment. We will show various examples for ligand exchange and encapsulation of quantum dots, plasmonic and magnetic nanocrystals. As a result, we will present smart nanocomposite materials with outstanding mechanical properties and switchable functionality as well as nanocrystals with adjustable bioresponse.

COLL 455

Surface peptide mediated quantum dot/ gold uptake

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The packing of biological molecules at a nanoparticle surface, whether an emissive QD or a non-emissive AuNP, can have profound effects on the uptake and processing of the package by a mammalian cell. In this presentation we will explore cell specific uptake patterns in multiple drug resistant (MDR) cancer cells and in STEM cells. The selective uptake patterns provide insights into the nature of the process.

COLL 456

Influence of composition and surface state on the toxicity and fate of indium phosphide quantum dots

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Colloidal semiconductor nanocrystals (quantum dots) possess unique optical properties, which make them attractive emitters for diverse applications such as optoelectronic devices or biomedical applications. During their life cycle, aging of quantum dots can lead to their dissolution and induce high toxicity due to the release of toxic chemical compounds. In this context In-based QDs have been proposed as less hazardous than the more popular Cd-based QDs. We compared the toxicity and fate of In-based QDs, either in their pristine form, or after artificial weathering in a climatic chamber. These QDs had an alloyed core composed of InZnP or InPZnS, and a gradient shell composed of Zn(Se,S). They were transferred from the organic to the aqueous phase using either penicillamine or glutathione as novel surface ligands. First, the kinetics of the QD physicochemical transformations during the aging process were studied by means of photophysical characterization. The major transformation products were identified using X-ray absorption spectroscopy and scanning-transmission electron microscopy coupled to energy-dispersive X-ray spectroscopy. Second, the toxicity of these QDs was evaluated in vitro on primary human keratinocytes, and in vivo using the freshwater polyp Hydra Vulgaris as model organism. Our results indicate that the physicochemical transformation of QDs in the climatic chamber is very rapid, with a total transformation occurring during the first two hours of ageing. Transformation occurs via both dissolution and precipitation of large aggregates where Se and S segregate from In, P, and Zn. The transformation products are much more toxic than pristine QDs. Core/shell QDs are safer than core QDs, and QDs with a core composed of InPZnS appear to be slightly safer than QDs with a core composed of InPZn. On the other hand, the nature of the surface ligand has no detectable influence on QD toxicity. Importantly, also in Hydra tissues speciation using XANES confirms the fast dynamics of QD degradation. Both InP-based core and core/shell QDs are far less toxic compared to penicillamine coated CdSe/ZnS QDs and their stability can be increased by growing on top of the gradient shell an additional ZnS shell.

COLL 457
Multiply-binding polymeric imidazole ligands: Influence of molecular weight and monomer sequence on colloidal quantum dot stability

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Colloidal semiconductor quantum dots (QDs) are attractive materials for bio-imaging and sensing applications due to their favorable optical properties. To be compatible with biological environments, the QD surface must be passivated by appropriate coatings, such as hydrophilic polymers, that promote colloidal stability and help to maintain the quantum yield, while resisting nonspecific interactions. Multiply-binding copolymer ligands in particular have proven to be effective in achieving QDs that exhibit low nonspecific binding and low acute toxicities, however their resistance to interference from endogenous molecules is still of concern. We assessed the stability of core/shell CdSe/Cd$_x$Zn$_{1-x}$S QDs coated with imidazole-bearing polymeric ligands in the presence of L-glutathione (GSH) under neutral conditions by means of photoluminescence and absorption spectroscopy. In particular, we synthesized copolymer ligands with different molecular weights in block and random sequences containing imidazole and poly(ethylene glycol) side chains on a methacrylate backbone via reversible addition-fragmentation chain transfer (RAFT) polymerization. This allows us to evaluate the influence of length and monomer sequence on QD stability. Introduction of GSH, an endogenous monothiol, to the polymer-coated QDs led to a reproducible change in PL quantum yield. The PL change was greatly diminished for block copolymers versus random copolymers of similar molecular weight and composition. Additionally, higher ligand populations were found on initial purification of block copolymer-coated QDs versus the random copolymers. We demonstrate that GSH does not significantly displace the polymers from the QD surface, suggesting that PL changes are driven primarily through ligand association. The block copolymers are more resistant to glutathione association —and indeed stronger binders— than the randomly-ordered copolymers, with higher molecular weight contributing to increased stability in both cases. To the best of our knowledge, this is the first study to directly compare the relative stability of block and random polymeric imidazole ligands.

COLL 458

Combining electrospray ionisation deposition and scanning tunnelling microscopy to investigate the surface assembly of macromolecules

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The ultimate spatial resolution of scanning tunnelling microscopy (STM) has allowed to gain an exceptional insight into the structure and the intra- and inter-molecular bonding of a huge number of adsorbed molecular system. Unfortunately, these remarkable analytical capabilities are achieved only under ultrahigh vacuum (UHV) conditions and
therefore cannot be directly applied to more interesting systems composed of functional (bio)molecules or complex synthetic compounds. In fact, thermal sublimation is the strategy of choice for preparing ultrathin films of small and heat-resistant molecules in UHV but larger, complex (bio)molecules are not compatible with this process. This challenge has been overcome in recent years by adapting soft-ionisation techniques developed in mass spectrometry (mainly electrospray ionisation, ESI) to transfer intact fragile molecules into the gas phase and to soft-land them onto atomically flat and clean substrates. When combined with advanced scanning probe microscopes operating under UHV conditions, these novel set-ups allow the surface deposition and high-resolution characterisation of a wide range of functional organic molecules and inorganic nanoparticles.

This talk will present recent advances in the development of ESI-deposition techniques and their combination with UHV-STM to analyse complex (bio)molecule-surface systems. It will start by reviewing the limits that standard molecular deposition imposes on the size of (bio)molecules that can be studied in surface science. It will continue by presenting a recently developed ESI-deposition setup based on a simple, efficient and modular design with a high intensity and mass selectivity. The discussion will then proceed to the application of ESI-STM to the characterisation of adsorbed polypeptides and polymers. In particular, it will be shown that this technique allows the imaging of individual macromolecules with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

**COLL 459**

**Programmable supramolecular self-assembly of DNA at surfaces**

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Supramolecular self-assembly on solid surfaces not only simplifies purification and facilitates integration with devices, but also offers new ways to integrate bottom up with top down to create multiscale functional architectures. However, existing successes in self-assembly at surfaces are limited to relatively simple structures made of only a few unique components. Moreover, due to the complex interplay between molecule-molecule interactions and molecule-surface interactions, the development of design rules that allow one to predictably form a wide range of patterns has been a formidable challenge. In contrast, DNA nanotechnology has enabled self-assembly of complex designer structures in the solution phase. In particular, the DNA origami method programmably forms complex nanoscale shapes by folding a long single-stranded DNA with hundreds of unique short DNA staple strands. The difficulty in forming complex structures at surfaces/interfaces is likely connected to attractive interactions that are needed to confine the structures to the surface. However, the precise roles of such interactions in the self-assembly of complex biomolecular structures are not known. Here we studied the staple-assisted folding of ssDNA scaffolds end-tethered to a dynamic surface, a self-assembled monolayer that allows us to precisely regulate the DNA-surface interactions on demand. The results provide direct evidence that attractive
non-specific interactions hinder DNA origami formation by restricting conformational freedom. In the presence of short-range repulsive interactions, both the folding kinetics and folding pathways are similar to those in the solution phase. The knowledge has allowed the surface to mediate the site-specific formation of DNA origami for the first time. We demonstrate that information encoded into a single surface-tethered molecule (seed strand) could initiate self-assembly of DNA origami of prescribed size, shape, and internal arrangement. Our approach offers a novel pathway to integrate bottom up DNA self-assembly with top-down techniques.

**COLL 460**

**Diverse self-assemblies of protein 2D crystalline at solid-liquid interface**

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Bio-diversity is the greatest strength in nature to make sure the prosperity and sustainable development of the earth and human society. On molecular scale, the diversity of proteins is one key to guarantee such bio-diversity. It is not just from the variety of amino-acid sequence, but also comes from the capabilities of proteins to adapt various structures and matrixes to response environmental stimuli. Inspired by nature, various strategies, like symmetric fusing-based crystallization, disulfide-bond based crystallization, and metal-ion-coordination-bond based crystallization, have been developed to construct protein crystals in bulk solution. However, the knowledge and approach to design single type of protein molecule with response to environment stimuli to express diverse self-assembly matrixes are still limited.

In this presentation, I will present the work to assemble the variant of L-rhamnulose-1-phosphate aldolase (RhuA), with incorporated Cys mutants, C⁹⁸RhuA, into different crystalline 2D arrays on solid-liquid interface. I have found that solvent mediated protein-surface interactions can alternate the energy-landscape of protein self-assembly from that in bulk. I am able to stabilize the quasi-stable intermediate phase of protein 2D assembly at solid-liquid interface. Furthermore, new assembly structure of C⁹⁸RhuA that does not exist in bulk has been created at the solid-liquid interface. In the end, the crystallization of the diverse crystalline and roles of substrate and solvent have been discussed in detail. All the findings inspire the novel strategy to create various protein assemble matrixes with single type of protein building unit. They also remind us the importance of solvent mediated surface to tune the self-assemblies of protein 2D structures both in nature and in human manners.

**COLL 461**

**Molecular mechanism of peptide assembly propensity studied with STM**
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Peptides and proteins are known to form a variety of ordered structures via assembling processes. The molecular insights of the assembly propensities of various peptide-based nanostructures are keen to the pharmaceutical studies and pathological analysis for neurodegenerative disorder processes such as Alzheimer’s disease (AD). Documented experimental results have revealed that the capability of peptides to form ordered structures has significant dependence on the sequence and composition of amino acids. An important subject under study is the formation mechanisms of peptide assemblies at the level of individual amino acids. We have endeavored to investigate the assembly propensity of peptides based on the high resolution structural analysis of surface-bound peptide assemblies by using scanning tunneling microscopy (STM). Specifically, the dependence of the peptide assembly structures on sequences will be pursued, including the impact of amino acids on the adsorption stability and assembly propensity. It may be anticipated that these efforts could advance the fundamental mechanism underlying the peptide assembly propensity, as well as provide the potential venues for developing novel diagnosis and therapeutic approaches towards relevant diseases.

COLL 462

Chiral organization and charge redistribution in molecular layers on surfaces beyond the monolayer

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The physicochemical properties of organic/metal interfaces are non-trivially influenced by the interplay of attractive/repulse interactions operating at different length scales. Molecular self-assembly on surfaces is thus governed by the strength of the molecule–molecule and molecule-substrate interactions, providing a hierarchy of structures. Extending the growth into the third dimension perpendicular to the substrate and/or the use of multicomponent heterostructures add a higher level of complexity.

The first part of this talk addresses the nontrivial effect of molecular dipoles on the surface work function of metals beyond the first layer. As a model system we have selected chloroaluminum phthalocyanine (ClAlPc) on Au(111). ClAlPc is a non-planar phthalocyanine with electric dipole moment perpendicular to the molecular plane, which can adopt two distinct configurations (Cl-up and Cl-down) when adsorbed on surfaces. By means of scanning tunneling microscopy (STM) and frequency modulation atomic force microscopy (AFM) under ultra-high vacuum (UHV) conditions, we investigate how the orientational order of ClAlPc affects the molecular organization and the local work function beyond the first layer. We demonstrate that the deposition of the second layer induces an important electronic and mechanical decoupling of the first layer from the surface, leading to a significant charge rearrangement beyond the first layer. The impact
of the orientational order of CIAIPc on the growth and organization of C60 on top is discussed.

The second part of this talk focusses on the self-assembly of two enantiomers with the purpose of exploring the origin of chirality transfer relevant for the bottom-up crystallization of 3D chiral assemblies. The assembly of two diphenylethlenediamine enantiomers, separately deposited on Cu(100), is investigated from the first stages of two-dimensional crystallization to the nucleation and growth of the second layer. We show that the chirality of enantiomers is expressed at different levels of molecular organization.

COLL 463

Building the next layer

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Supramolecular self-assembly of monolayers on planar surfaces provides access to remarkably complex surface architectures. Application of such patterned monolayers as templates to build designer materials into 3D is one focus of current research. This presentation will describe the use of “non-morphology determining” reactive groups within self-assembled monolayers to direct chemistry that builds (and patterns) the next layer(s).

COLL 464

Sub-molecular tunneling barrier measurements of molecular adlayers at the solution-graphite interface

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Scanning tunneling microscopy (STM) was used to probe electron-tunneling barriers for molecular monolayers physisorbed onto the surface of highly oriented pyrolytic graphite using the tip modulation method. In this way direct comparisons were made between the typical topographical data and the tunneling barrier measurements. Measurements were conducted for non molecular orbital (MO)-mediated tunneling (in the case of monolayers of stearic acid), as well as MO-mediated tunneling (in the case of monolayers of a planar polycyclic aromatic compound, indolo[2,1-b]quinazoline-6,12-dione, aka tryptanthrin). For the non MO-mediated tunneling case, the barrier height map was observed to correlate with the electrostatic potential (ESP) of the adsorbed molecules; indeed, the effects of the ESP distribution were used to interpret previously
unreported subtle differences between two different conformers of stearic acid adsorbates. For the MO-mediated tunneling case, the barrier height map was observed to correspond to the spatial properties of the MO directly, with little correlation to the ESP distribution of the molecule, as indicated by excellent agreement of the experimental data with STM barrier height simulations developed by the authors from density functional theory computational results of the molecules themselves.

COLL 465

Understanding cooperative interactions in the polymorphs of self-assembled macrocycles

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Understanding the fundamental molecular interactions underpinning self-assembly is a crucial component for the design of self-assembled supramolecular architectures over varied length scales having defined function and composition. Recent experimental observations using STM on the self-assembly of tricarbazole triazolophane macrocycles (tricarb) show the existence of both ordered honeycomb and non-ordered structures at the solution/HOPG surface. Here, we have performed a comparative analysis of three different structural motifs for the self-association and growth of tricarb oligomers using dispersion-corrected density functional theory on appropriate cluster models based on the experimental findings. Our analysis shows a positive cooperativity of the H-bonding contributions to the interaction energies from favorable local dipole orientations from triazole units of the self-assembled molecules. Effective parameters obtained from our theoretical calculations are used to explain the experimentally observed structures, and provide detailed insights into the effect of intermolecular dipole-dipole interactions on the self-assembly process.
Order/disorder phase boundary in supramolecular self-assembly of macrocycles at surfaces

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Self-assembly of tailored organic molecules at surfaces offers a route to multifunctional thin films where the structure can be steered by external stimuli to express different functions. Programming the packing structure is essential for controlling the function of the material. Here, we study self-assembly of a series of tricarbazolo triazolophane macrocycles (tricarb) on graphite. Scanning tunneling microscopy at the liquid/solid interface reveals that tricarb can self-assemble into a disordered (higher entropy) packing structure with randomly oriented molecular components or a crystalline honeycomb lattice (lower entropy). Through systematic variation of the peripheral functional groups, solvent, concentration, and temperature, we are able to determine rules for controlling the system between the disordered and ordered states. Interestingly, shifts in this parameter space that tend to increase the entropy of the overall system lead to better ordering at the surface. This can be rationalized as a shift in adsorption/desorption equilibrium to favor either a low density surface structure with more tricarb in solution or a higher density surface structure. This unusual observation highlights the complexity of self-assembly at surfaces and how seemingly minor alterations in molecular components can be amplified into large effects on self-assembly, which we expect to translate into function.
COLL 467

Multi-layered metal-organic framework microcrystals as a host to control the guest-to-host and guest-to-guest interactions

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A bio-inspired design of using metal-organic framework (MOF) microcrystals with well-defined multi-layered structures was used as a matrix to host multiple guests including molecules and nanoparticles at separated locations to form a hierarchical material, mimicking biological structures. The interactions such as energy transfer (ET) between different guests are regulated by precisely fixing them in the MOF shells or encapsulating them in the cavities between the MOF shells. We could selectively establish or diminish the guest-to-framework and guest-to-guest ET. This work provides a platform to construct complex multifunctional materials, especially those need precise separation control of multi-components.

COLL 468

Nanostructured electrode materials for Li/Na ion storage
Among various electrochemical energy storage technologies, lithium ions batteries were considered as most practical ones due to their high energy densities and high stability. Recently, Na-ion batteries (NIBs) have attracted great attention because of the abundance of sodium and low cost in comparison to lithium ion batteries. However, NIBs still have many technical issues, such as larger volume change of the electrode materials, lower specific capacities, poorer rate capability, as well as shorter cycling life due to larger ionic radius and molar mass of Na\(^{+}\) ions than that of Li\(^{+}\) ions. We will present our recent activities on synthesis of nanostructured electrode materials for Na/Li ion storage applications. We carried out works on phosphate\(^1\), \(V_{2}O_{5}\), \(Na_3V_2(PO_4)_3\) (NVP)\(^2\), black phosphorus (BP), and sulfides by various preparation process. From materials design point of view, we aim to increase the specific capacity, volumetric capacity, 1st-cycle Coulombic efficiency, cycling life and rate performance. Many of these materials show high cycling stability and good rate capability, which is suitable for high power and fast charging applications.

**COLL 469**

**Advanced in situ X-ray diffraction in revealing the structural changes of high voltage cathode under the effect of different electrolytes**

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Fluorinated electrolyte is a promising candidate to replace the regular carbonate based electrolyte because of its impressive anodic stability, conductivity as well as thermo-stability. Yet, most of the fluorinated electrolyte studies focused on the interfacial reaction and electrochemical performance. Although it is equally critical in understanding the interaction between different electrolyte systems and the bulk cathode structure to improve the energy density of the whole cell, the research regarding this topic is limited. In this work, bulk electrode analysis via *in-situ* XRD technique was carried out to unveil the high Nickel cathode structural changes by using different electrolytes and the results indicate the use of fluorinated electrolyte can mitigate the electrolyte decomposition. Most importantly, it can also assist the preservation of the crystal structure of high Nickel cathode by inhibiting the loss of active Li ion and transition metal during cycling. All results converge to the conclusion that the use of fluorinated electrolyte can not only stabilize the interface but also conserve the bulk structure.

**COLL 470**

**From interfacial studies to high-performing catalysts: Synthetic design at nanoscale**
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Material formation in nature is precisely controlled in all aspects from crystal nucleation, growth to assembly to deliver superior functions. Specific biomolecule-material interactions have been hypothesized to play important roles in these processes. Proteins, polymers and small molecules have been extensively explored to replicate the degree of control in material formation in vitro and for nonbiogenic materials. In this talk I will share our efforts on decoding the myth of biomolecular specificity to material surface and their roles in controlling crystal growth and assembly. I will talk about our recent efforts on improving catalytic functions of nanocrystals through synthetic design based on specific peptide-surface interfacial interactions. In specific I will share the first-time peptide guided assembly of ultrathin Pt nanoplates as an efficient electrocatalyst, which exhibits dramatically improved activity toward both ORR and HER when compared to current state of the art commercial Pt/C electrocatalysts.

COLL 471

Toward total synthesis of thiolate-protected metal nanoclusters

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Total synthesis, where desired organic- and/or bio-molecules could be produced from simple precursors at atomic precision and with known step-by-step reactions, has prompted centuries-lasting bloom of organic chemistry since its conceptualization in 1828 (Wöhler synthesis of urea). Such expressive science is also highly desirable in nanoscience, since it represents a decisive step towards atom-by-atom customization of nanomaterials for basic and applied research. Although total synthesis chemistry is less established in nanoscience, recent years have witnessed seminal advances and increasing research efforts devoted into this field. In this talk, I will discuss our recent work on introducing and developing total synthesis routes and mechanisms for atomically precise metal nanoclusters (NCs). Due to their molecular like formula and properties (e.g., HOMO-LUMO transition, strong luminescence and stereochemical activity), atomically precise metal NCs could be regarded as “molecular metals” (or metallic molecules / molecular-like metals), holding potential applications in various practical sectors such as biomedicine, energy, catalysis and many others. More importantly, the molecular-like properties of metal NCs are sensitively dictated by their size and composition, suggesting total synthesis of them as an indispensable basis for reliably realizing their practical applications.

COLL 472

Synthesis and functionalization of NIR-to-NIR upconversion nanophosphors for oil reservoir application
Nanomaterials with efficient up-conversion (UC) luminescence have great potential in applications for optical imaging, biomedical labeling, solar cells and photocatalytic devices, etc., but have not been used in oil and gas industry yet. Currently, the most efficient and intense up-conversion luminescence is from near infrared (NIR) to visible by using the combination of an Yb$^{3+}$ sensitizer (absorber) and an RE$^{3+}$ ($\text{Er}^{3+}$, $\text{Ho}^{3+}$ or $\text{Tm}^{3+}$) activator (emitter) in host materials. These phosphor materials usually have multiple emissions with blue, green and/or red emissions, and intensity ratios of the multiple emissions are dependent on the efficiency of quenching processes, however, it is still a challenge to fabricate nanophosphors with nearly or fully pure upconversion emission in desired spectral windows. For different applications, defined emissions at certain wavelengths are required. For example, nanophosphors with near-infrared to near-infrared (NIR-to-NIR) upconversion have clear advantage with a petroleum clear optical window. In this research, by manipulating content of Yb$^{3+}$/Tm$^{3+}$ in selected host materials, we have successfully synthesized rare earth ions codoped nanoparticles via wet-chemical method and obtained nearly pure NIR-to-NIR upconversion photoluminescence. A surface functionalization procedure has been also developed to stabilize the nanoparticles in high temperature and high salinity environment. Both the emission light at ~800 nm and the excitation at 980 nm are in petroleum clear spectral range, so that they have enhanced penetration and eliminated background interference in crude oil-brine mixtures. The novel upconversion nanoparticles can be used as new tracer nanoagents for better understanding water flooding and enhanced oil recovery process in reservoirs.

**Coll 473**

Investigating the effects of phase transfer procedures on the photoluminescence of aqueous quantum dots

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Bright, stable, and monodisperse colloidal semiconductor nanocrystals, or quantum dots (QDs), are typically synthesized in organic solvents. These synthesis protocols produce QDs with organic ligand shells, which render them insoluble in aqueous environments. Post-synthetic ligand exchange procedures replace organic ligands with water-soluble ligands, such as mercaptopoalkanoic acids, and allow QDs originally synthesized in organic solvents to be dispersed in water. Despite the widespread use of these phase transfer procedures, their effects on QDs are poorly understood. Herein, we investigate the effects of phase transfer procedures on the photoluminescence (PL) of aqueous mercaptoalkanoic acid-capped lead sulfide (PbS) QDs. We report a bathochromic shift of the PL of PbS QD ensembles as a function of solution pH. The magnitude of the PL spectrum shift correlates with the polydispersity of the ensembles after phase transfer into water. The results of spectroscopic and scattering experiments, along with
interparticle interaction calculations and computer simulations, suggest that the bathochromic shifts are the result of energy transfer within PbS QD assemblies that form as the solution pH decreases. This system is a model for spectroscopically monitoring the success, quality, and reproducibility of phase transfer procedures, which are critically important for producing high-quality aqueous QDs for applications in photocatalysis and biological sensing.

**COLL 474**

**Design efficacious targeting lipid nanoparticles**

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Bicelles can form in a mixture composed of long- and short- lipids with an appropriate molar ratio (i.e., long-to-short) ranged from 2 and 6, and they are able to encapsulate lipophilic molecules in the hydrophobic region. It has been proved that at low lipid concentration bicelles undergo an irreversible disc-to-vesicle transition with increased temperature. Previously, enhanced cellular uptake was found for the discoidal bicelles compared to the vesicles of the identical chemical composition. In this presentation, we will show Nile red and meta-tetra(hydroxyphenyl)chlorin (a photodynamic therapeutic agent) can be entrapped in the bicelles. Moreover, a PEGylated lipid with folate functional group can anchor in the surface of bicelles providing targeting effect to KB cancer cells. A consistent trend is found for the in vitro and in vivo efficacy: folate-discs > folate-vesicles > non-folate-discs > non-folate-vesicles. The advantages of bicelles as nanocarriers including highly biocompatibility, well-defined size, robust formation, easy encapsulation of hydrophobic molecules (therapeutics and/or diagnostics) and scalable one-pot synthesis. Therefore, they can serve as a generalized in vivo multi-modal delivery platform.
Assembly of receptor tyrosine kinases in the plasma membrane regulates function at the protein, cell and organism levels

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Chemical complexity in the plasma membrane drives organization and dynamics at multiple time and length scales. The focus here will be on how this complex environment regulates specific protein-protein interactions for representative members of the receptor tyrosine kinase (RTK) family of membrane proteins. RTKs have a ligand-binding extra-cellular domain connected to an intra-cellular kinase domain through a single pass transmembrane helix. Assembly of RTKs into dimers, tetramers and higher order multimers is connected to receptor activation, which ultimately guides cellular function. To monitor RTK assembly in the live cell plasma membrane we use pulsed-interleaved excitation fluorescence cross-correlation spectroscopy (PIE-FCCS). PIE-FCCS monitors several physical parameters like mobility, concentration, proximity, and
dimerization/multimerization. Recently we have shown a functional dependence between the degree of cross-correlation and the oligomerization state of the protein in the plasma membrane. This allows us to measure pairwise associations between RTK’s and determine how they are modulated by ligand activation and co-receptor associations. Recent data will be shown for two receptors, EphA2 and EGFR, which have adopt very different ligand-free and ligand-bound oligomerization states. With a series of point mutations we show that these assembly states regulate receptor function in cells and tumor growth in vivo.

COLL 476

Mechanism of toxin enrichment in bacterial outer membrane vesicles

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Gram-negative bacteria release nanoscale vesicles called outer membrane vesicles (OMVs) throughout growth to serve various functions, including delivery of toxins to both host and bacterial cells. Although the OMV is derived directly from the bacterial outer membrane (OM), numerous reports have demonstrated that the protein composition of the OMVs and OM can differ substantially. In particular, bacterial toxins are often reported to be enriched in the OMV relative to the OM. We undertook a series of studies to investigate the process by which a bacterial toxin, leukotoxin (LtxA), produced by the Gram-negative bacterium *Aggregatibacter actinomycetemcomitans*, is sorted to OMVs. This toxin is secreted via a one-step Type I secretion system across both the inner and outer membrane, but has been reported to re-associate with the bacterial OM. Our results demonstrate that LtxA is associated with the outer surface of the OMV and is enriched in the OMVs. We identified two populations of OMVs, one highly abundant population with diameters of approximately 100 nm, and a smaller population with diameters of approximately 350 nm. The small OMVs are produced throughout bacterial growth, while the large OMVs are produced only during later phases of growth. Interestingly, our results suggest that LtxA is only associated with the large OMVs. Because LtxA expression does not begin until later phases of growth, we hypothesized that LtxA itself might induce OM membrane curvature, thus promoting OMV budding. Instead, we found that variations in the lipopolysaccharide, present on the outer leaflet of the OM and OMV, drive both OMV formation and LtxA association with OMVs. Together, these results demonstrate a mechanism by which a bacterial protein (toxin) is sorted to secreted vesicles due to variations in its membrane affinity.

COLL 477

Spin labeling of cysteines for EPR structural studies on type II cannabinoid receptor CB$_2$
The CB$_2$ receptor is a rhodopsin-type G protein-coupled membrane receptor (GPCR) that signals via inhibition of adenylyl cyclase by G$_{i\alpha}$/G$_{o\alpha}$ protein subunits, while G$_{\beta\gamma}$ subunits signal via mitogen-activated protein kinases (MAPK) and extracellular signal-regulated kinases (ERK) pathways. The CB$_2$ receptor is primarily located in cells of immune and hematopoietic systems such as thymus, spleen, and tonsil. It plays a major role in inflammatory processes in a variety of organs including liver, kidneys and the gastrointestinal system and has become a valuable target for pharmaceutical intervention. The goal of the project is to follow structural changes of the receptor upon interaction with ligands and other interaction partners of the signaling pathway by selective spin labeling of reactive cysteines followed by electron paramagnetic resonance (EPR) spectroscopy. Wild type CB$_2$ receptor contains 13 cysteine residues, eight of which with expected exposure to an aqueous environment, and the rest located in transmembrane domains. Two of the three cysteines in extracellular loop EL$_2$ form a disulfide bond which stabilizes the tertiary structure. The CB$_2$ receptor is expressed as fusion with maltose binding protein and two affinity tags in *E. coli* cells and purified in detergent solution. A minimum cysteine mutant of CB$_2$ was developed that showed insignificant functional impairment only as judged by ligand binding and G protein activation as well as much reduced activity for chemical labeling of cysteines. Single cysteine residues in water exposed regions of the receptor were reintroduced and mutants characterized by labeling efficiency and protein function. Spectra are analyzed in terms of polarity of label environment and immobilization of label movements as well as sensitivity to structural changes triggered by ligand binding. Results may yield a deeper functional characterization of endogenous and synthetic cannabinoid ligands important for biomedical applications.
was obstructed by the domains, and the spreading velocity linearly decreased with the polymer fraction, reaching the percolation threshold. Self-spread lipid bilayers had a higher density of lipids than those formed by the spontaneous rupture and spreading of vesicles (vesicle fusion), as determined by the fluorescence intensity of laurdan.

Detergent-solubilized rhodopsin from bull frog could be reconstituted into the self-spread membrane. Preparation of supported membranes by the self-spreading provides several advantages compared with those formed by the vesicle fusion. First, self-spread bilayers have higher packing of lipid molecules, since lipids are continually supplied from the reservoir. It should lead to a lower susceptibility to defects formation upon membrane protein reconstitution using detergents. Second, lipid reservoirs can be kept in a dried state until use, which enables a multiplex array of printed lipid membranes to be stored and used onsite.

COLL 479

Fatty acids of Gb₃ influence its partition in phase separated lipid membranes as well as Shiga toxin binding

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The Shiga toxin B subunit (STxB), which is involved in cell membrane attachment and trafficking of Shiga holotoxin, binds specifically to the glycosphingolipid Gb₃. In biological membranes, Gb₃ glycosphingolipids differ in their fatty acid composition and there is strong evidence that the fatty acid alters the binding behavior of STxB as well as the intracellular routing of the Shiga toxin/Gb₃ complex. By means of chemical synthesis, Gb₃ species with different fatty acids as well as fluorescently labeled compounds have become accessible enabling us to investigate the influence of the fatty acid on the partition of Gb₃ in liquid-ordered (lₒ)/liquid-disordered (l_d) phase-separated lipid bilayers and how this partition influences Shiga toxin binding. Three different model membrane systems were applied, namely giant unilamellar vesicles, supported lipid bilayers as well as pore-spanning membranes. Our results obtained using the different model membrane systems clearly demonstrate that the fatty acid of Gb₃ significantly impacts the overall phase behavior of the membranes. Moreover, the lateral organization of STxB bound to the membranes is influenced by the Gb₃ species, which is discussed in the context of Shiga toxin induced invaginations and its internalization into the cell.
Peering into the lipid world

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Lipids remain one of the most enigmatic classes of biological molecules. Lipids were likely one of the first components necessary for life, yet our understanding of how lipid membranes could have arisen spontaneously is a mystery. Human cells produce thousands of unique lipid species, but the purpose for such diversity remains unknown. Dysregulation of lipid metabolism is a key factor in some of the most common diseases that afflict human beings. My lab is using imaging and chemistry to understand the assembly and function lipids. We are watching the formation of artificial cells that consist of synthetic membranes that can continually reproduce. We are designing specific chemical reactions to manipulate and image lipids within living cells during cell death and disease. Our ultimate goal is to answer fundamental questions about the origins of lipid membranes and build a functional understanding of the diverse array of lipids present in life today.

COLL 481

Lateral diffusion and fluorescence quenching in lipid bilayer membranes on graphene oxide

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Lipid bilayer is a fundamental structure of plasma membranes, and plays important roles for various membrane reactions such as the transport of material, energy, and information. Graphene oxide (GO) is an amphiphilic atomic sheet, and shows a unique fluorescence quenching property. In this study, we formed supported lipid bilayers (SLB) on GO, and investigated the lateral molecular diffusion and fluorescence quenching efficiency with the single particle tracking (SPT) method. We formed the SLB comprising of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), polyethylene glycol-1,2-disterol-sn-glycero-3-phosphoethanolamine (PEG-DSPE) and 1,2-dipalmitoyl-sn-glycero-3-phosphoethanol (DPPTE) by the vesicle fusion method. The GO suspension was prepared by the modified Hummer’s method, and was dropcast on a thermally oxidized SiO2/Si substrate. A carboxyl-coated quantum dot (Qdot) conjugated to the SLB containing DPPTE with a maleimide-hydrazide heterocross-linker. We measured the diffusion coefficient (D) of the conjugated Qdots on SLB on GO by SPT. Fluorescence dyes are not available under the quenching effect of GO, but Qdot was bright enough for SPT measurement on GO. We analyzed the Qdots diffusing the GO and GO-free SiO2 region, and evaluated D in each region. The SLB on GO had ~30% smaller D than that on the GO-free SiO2 region. The quenching efficiency on GO, which was calculated from the fluorescence intensity of Qdots on GO, indicated the layer numbers of bilayer on GO.
Domain dynamics and shape adaptations in osmotically stressed giant lipid vesicles

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A solute, excluded from or confined within a spatial "compartment" embedded in an aqueous continuum, creates a gradient in the chemical activity of water. This in turn prompts a directed flow of water pushing it into the solute-laden compartment and out of the solute-starved one. Serving as a non-specific entropic force, this osmotic stress acts on the vesicular boundaries producing long-lived out-of-equilibrium morphologies and cooperative behaviors.

Drawing from recent experiments in our lab employing giant vesicles containing (or excluding) molecular (e.g., sugars) and colligatively non-ideal macromolecular (e.g., PEG and Dextran) osmolytes, this talk considers how the osmotic activity of water dynamically remodels the membrane. It highlights experimental observations of shape adaptations (including protrusions, invaginations, and buds) and topological division (producing colonies of daughter vesicles) when subject to hypertonic bath and examines the domain dynamics under hypotonic bath.

Supramolecular, chemistry-based, reversible surface charge reversal

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The properties of nanomaterials are largely dependent on the size and morphology of nanoparticles, as well as on their organization within nanostructured materials. A large number of synthetic methods have been developed, which allow an exquisite degree of control over these parameters. One of the most important factors behind particle growth and interparticle interactions is the chemical composition of the nanoparticles’ surface, which often involves the presence of organic ligands, usually surfactants or polymers. These ligands can be used to protect specific crystallographic facets in nanocrystals, to facilitate binding to other molecules or surfaces, but also to direct the assembly of the nanoparticles into well-defined nanostructures.

We describe an approach to regulate the surface charge on gold nanoparticles, using supramolecular chemistry. The strategy relies on the functionalization of AuNPs with negatively charged pyranines, which largely hamper their penetration in cells. Cellular uptake can be activated in situ through the addition of cationic covalent cages that specifically recognize the fluorescent pyranine dyes and counterbalance the negative charges. The high selectivity and reversibility of the host-guest recognition activates
cellular uptake, even in protein-rich biological media, as well as its regulation by rational addition of either cage or pyranine.

**COLL 484**

**Competing role of surface chemistry on nanostar stability and SERS activity**

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interfaces. In techniques such as surface-enhanced Raman scattering (SERS), molecules must interact with the metal surface at short distances of 2 nm or less. For non-thiolated molecules, these interactions are energetically unfavourable because of ion stabilization, surface solvation, and/or competition with other molecules in the system. These effects often lead to unsuccessful detection using SERS. Herein, the surface chemistry of HEPES synthesized and stabilized gold nanostars are evaluated as a function of pH using both computation and spectroscopic methodologies. The binding affinity and structure of HEPES on gold nanostars is largely influenced by solution pH and the surface pKa of HEPES on gold relative to solution. This impacts the morphology, surface potential, and surface activity of the nanostars in SERS. These effects are monitored using time-dependent LSPR spectra and TEM analysis, which confirm that gold nanostars restructure upon acidification. Spectroscopic evidence supports that both the sulfonate and amines groups in the piperazine ring of HEPES can bind to gold but affinity of all of these interactions weaken upon acidification. DFT calculations support this binding interaction. Upon weakening of the surface stabilizing agent, gold nanostars can be used to detect small non-thiolated molecules. Notably, benzene, a molecule that interacts to gold through London dispersion forces only, successfully adsorbs to gold. The thermodynamics of benzene adsorption is monitored through SERS. Intermolecular interactions between both benzene and gold as well as benzene and benzene are observed and interactions quantified. As a result, we expect these studies will broaden the scope of SERS and plasmonic-based assays as small molecules with weak affinity to metal nanostructures will be more readily detected.

**COLL 485**

**Understanding the protein corona one molecule and one nanoparticle at a time**

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The fate of nanoparticles interacting with the environment including the human body depends strongly on the corona that forms after contact with proteins. It is well established now that this protein corona affects the biological interactions with cells as receptors recognize the adsorbed proteins rather than the nanoparticle core. However, much less understood is the time-dependent composition of the protein corona and any structural changes of the adsorbed proteins potentially altering their natural function or
leading to unwanted nanoparticle aggregation. While ensemble characterization techniques have been very powerful, they are often limited to ex-situ conditions. Here, we present our recent progress on characterizing the protein corona using powerful super-resolution single molecule fluorescence microscopy and various single particle spectroscopy including circular differential scattering.

COLL 486

Efficient plasmon-induced hot electron transfer at metal/semiconductor junctions

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It has been well-established that excitation of plasmons in metal nanostructures can lead to the injection of hot electrons into semiconductors or adsorbed molecules, which can be used to enhance photocatalysis. This novel mechanism suggests that plasmonic nanostructures can potentially function as a new class of widely tunable and robust light harvesting and catalytic materials for solar energy conversion. More importantly, it provides a novel approach to access highly energetic and reactive states of metals that is difficult to access with thermal chemistry. However, plasmon-induced hot electron injections from metal to semiconductor or molecules are still inefficient because of unfavorable initial hot electron distribution and the competing ultrafast hot electron relaxation processes within the metallic domain.

In this talk, we discuss two approaches to enhance the efficiency of plasmon induced hot electron transfer. In the first approach, we explore the possibility of enhancing hot electron distribution by decreasing the size of plasmonic Au particles. Using CdS/Au nanorod heterostuctures, we show that the hot electron injection efficiency increases at smaller Au particle size. We attribute this size dependence to increasing contribution of surface assisted plasmon damping, which generates more hot electrons compared to damping by interband transition. In the second approach, we demonstrate that in CdSe/Au hetersostructures with strong metal/semiconductor coupling, the plasmon decays by direct excitation of an electron from the metal to semiconductor, i.e. plasmon induced interfacial charge transfer transition (PICTT). The new plasmon damping pathway can be very efficient because it bypasses the competition with hot electron relaxation within the metal satisfies both the energy and momentum conservation. We will discuss whether PICTT can be a general scheme for efficient hot electron transfer.

COLL 487

Direct Optical Lithography of Functional Inorganic Nanomaterials (DOLFIN) enabled by novel nanocrystal surface chemistry

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In recent years, solution-processed colloidal nanocrystals and quantum dots (QDs) have emerged as a versatile platform for building electronic and optoelectronic devices. These materials enable non-epitaxial deposition and low-temperature processing of light-emitting diodes, field effect transistors, near- and mid-infrared photodetectors, and solar cells. The transition from individual devices to the level of electronic circuits, sensor arrays, and electrically driven QD displays requires the development of material-adapted patterning methods, which was lagging behind. The lack of efficient methods for high-resolution and high-fidelity additive patterning of solution-processed electronic materials slows the transition from individual proof-of-concept devices to real-world applications. We introduce a new method for Direct Optical Lithography of Functional Inorganic Nanomaterials (DOLFIN), which uses inorganic nanomaterials with photochemically active surface ligands. This process combines multiple benefits of photolithography and is tailored toward efficient patterning of inorganic nanomaterials without diluting or contaminating them with organic photoresists and other byproducts. The range of materials that can be patterned using this new technique includes metals, semiconductors, oxides, as well as magnetic or rare earth compositions. Almost any inorganic nanomaterial can be converted into a photosensitive ink that can be directly patterned using DOLFIN. The ultimate lateral resolution of DOLFIN can extend down to about 30 nm and possibly below. No organic impurities are present in the patterned layers, which helps achieve good electronic and optical properties. The conductivity, carrier mobility, dielectric, and luminescence properties of optically patterned layers are on par with the properties of state-of-the-art solution-processed materials. The ability to directly pattern all inorganic layers using a light exposure dose comparable to that of organic photoresists provides an alternate route for additive device manufacturing.

**COLL 488**

**Optimization of the surface, ligands, and structure of semiconductor nanocrystal quantum dots (QDs) for photocatalytic charge transfer reactions**

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This talk focuses on the use of semiconductor nanoparticles or quantum dots (QDs) as the sole photocatalyst for photoinduced electron transfer (PET) reactions and the optimization of their surface, ligands, and structure to increase their viability as charge transfer catalysts. QDs have typically acted as sensitizers for separate, molecular or metal co-catalyst which restricts reactions to selected co-catalyst binding sites and sacrifices the high surface area native to these nanomaterials. Direct electron transfer from the QD, however, is limited as many reactions require multiple electrons transferred to a single substrate. We demonstrate that using phosphate ligands leads to “bare” QDs with underpassivated Cd(2+) atoms which can be reduced to form Cd(0) sites. These reduced surface states facilitate two-electron transfer reactions such as aldehyde or proton reduction while maintaining a high density of catalytic sites on the QD surface. We go on to investigate how QDs can act as the sole catalyst for
underexplored reactions such as light-mediated polymerization. Specifically, we show that QDs can mediate reversible addition-fragmentation chain transfer (RAFT) polymerization with living polymerization kinetics and high propagation efficiency. As polymerization only occurs with illumination, the reaction provides temporal resolution of polymer growth and a method for the synthesis of precise block copolymers as monomers can be replaced in the dark. Finally, we demonstrate that the nanoparticles can be easily removed which facilitates polymer purification and catalyst recycling, unlike molecular catalysts.

**COLL 489**

**Award Address (ACS Award in Colloid Chemistry sponsored by the Colgate-Palmolive Company). Tunable plasmonic nanoparticles: New materials and new applications**

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From the initial experimental realization of the idea that changing the shape of a metallic nanoparticle changes its color, the field of plasmonics has emerged as both a colorful and highly practical field of chemistry. While this field is rooted in the optical properties and chemistry of the noble metals, more recently, interest in more sustainable metals, such as Aluminum, has emerged. The synthetic chemistry of Aluminum nanocrystals, however, appears to be a unique chemical frontier in comparison with noble metal nanoparticle chemistry. We have begun to examine how the nucleation and growth of Al nanocrystals can be controlled by solvent complexation, and how the surface of Al NCs can be modified to control its properties even further. Al NCs provide their own unique surface chemistry to enable new properties of surface-enhanced Raman scattering, and provide a platform for the growth of functional surface layers such as metal-organic frameworks (MOFs). Earth-abundant plasmonic nanoparticles are playing an increasingly important role in photocatalysis, where, when combined with reactive species at their surfaces, they can lower the barrier to chemical processes when illuminated. This “antenna-reactor” structure has been shown to increase turnover rates and quantum efficiencies of chemical reactions while the reaction proceeds at far lower temperatures than under conventional thermocatalytic conditions.

**COLL 490**

**Award Address (ACS Award in Surface Chemistry sponsored by the Procter & Gamble Company) Models for heterogeneous catalysts: Complex materials at the atomic level**

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Understanding catalysis, and in particular heterogeneous catalysis, has been based on the investigation of model systems. The enormous success of metal single crystal
model surface chemistry, pioneered by physical chemists, is an outstanding example. Increasing the complexity of the models towards supported nano particles, resembling a real disperse metal catalyst, allows one to catch in the model some of the important aspects that cannot be covered by single crystals alone. One of the more important aspects is the support particle interface. We have developed strategies to prepare such model systems based on single crystalline oxide films which are used as supports for metal and oxide nano particles, whose geometric structure, morphology, electronic structure, as well as interaction and reaction with molecules from the gas phase may be studied at the atomic level.

After a general introduction to model studies in catalysis, results from different research areas are presented: 2D-3D-morphology, geometric, and electronic structure of supported metal nano particles in relation to reactivity of CO₂ as well as on two-dimensional silicates and reaction in confined space.

**COLL 491**

**Fabrication and flow characteristics of monodisperse bullet-shaped microparticles with controllable structures**

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The preparation of microparticles with non-spherical shapes has attracted increasing interest because the special physical properties of non-spherical microparticles can increase their performance in a wide variety of industrial applications and clinical pathologies. Here a simple and flexible approach is developed to fabricate monodisperse bullet-shaped microparticles with controlled structures from microfluidic droplet templates, which are deformed by shear stress from shear fluid and spatial confinement from microchannel. The deformation of droplet templates can be simply controlled by varying the flow rate of shear fluid and the inner diameter of shear tube. By scaling up the microfluidic device, bullet-shaped microcapsules with different internal structures can be easily fabricated from deformed double emulsion droplets. The results of flow characteristics show that, the bullet-shaped microparticles have a higher velocity than the spherical microparticles with the same volume if they flow in the microchannel with smaller diameter than the length of the bullet-shaped microparticles; whereas their flowing velocity is slightly lower than that of spherical microparticles in the microchannel if the channel diameter is larger than the length of bullet-shaped microparticles. In microchannels of a model device, bullet-shaped microparticles show better embolization performance than spherical ones. The bullet-shaped microparticles and microcapsules are promising as materials candidates in the fields of embolization therapy, substance transfer and drug release systems. The proposed strategy in this study provides a facile route for fabricating bullet-shaped microparticles with controlled structures and presents intriguing possibilities for growing researches including non-spherical microparticles and micromachine systems.
New insights to optical properties of fluorescent quantum dots by polarized resonance synchronous spectroscopy

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Nanocrystal fluorescent quantum dots (QDs) have been used in bio-imaging, disease diagnosis, lasing, and solar energy conversion. However, quantification of the optical properties of QDs are challenging with existing spectroscopic methods because of the complex interplay of the photon absorption, scattering, and emission that can concurrently occur in QD samples. Presented herein is the polarized resonance synchronous spectroscopic method and its application for quantification of the QD optical constants including absorption, scattering, and on-resonance-fluorescence (ORF) cross-section spectra as well as Stokes’-shifted fluorescence depolarization spectra. The ORF and light scattering contribution are separated in the polarized resonance synchronous spectroscopic (PRS2) spectra, and the UV-vis extinction spectra are decomposed into absorption and scattering components. The core-shell-ligand structured QDs with different shell volume and geometry are investigated. Scattering and absorption cross-section increased with increasing QD shell volume. The ORF cross-section monotonically decreases as the volume increases, indicating for a unit mass of QD, the increment of QD shell volume render the QD a stronger scatter and absorber, but a less efficient ORF emitter. The ORF quantum yield for rod-shape QDs (~10%) is significantly higher than that of the dot-shape QDs (<3%), which offers a new way to differentiate QD geometry. SSF depolarization is strongly dependent on the QD aspect ratio, which decreases from ~1 to ~0.6 when the aspect ratio changes from 1 to 16.8. The new insights provided by the presented technique relate the QD geometry to its optical properties, which can be constructive for QD design and in-situ monitoring QD synthesis.

Theoretical study of X-ray-Induced Energy Transfer (XIET) from nanomaterial donors to nanomaterial acceptors

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A systematic theoretical study was carried out here to investigate a new phenomenon of X-ray induced energy transfer (XIET) within the purview of X-ray nanochemistry. XIET occurs between a strongly X-ray absorbing nanomaterial such as one or more gold
nanoparticles (donors) and a weakly X-ray absorbing nanomaterial such as a hollow silica nanoparticle filled with water (acceptor), and part of the energy absorbed by the donors can be transferred to the acceptor when the two are positioned sufficiently close to each other and under 20–100 keV X-ray irradiation. XIET was studied as a function of dimension, composition, configuration and orientation of donors and acceptors, number of donors, and X-ray energy. Relative and absolute percentage XIET efficiencies were calculated. These results provide a theoretical framework to guide future experimental XIET studies.

COLL 494

*In-situ* analysis of nucleation and growth of transition metal oxalate precursor particles via time evolution of solution composition and particle size distribution

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The increasing demand on battery performance including energy density and cycle life requires more precise control over phase purity of the active materials and the electrode microstructures. Both of these properties are closely related to constituent particle composition and morphology. Coprecipitation is a popular synthesis route to produce precursors for electroactive, multicomponent transition metal oxides for many applications, including energy storage. Coprecipitation has advantages in that it is scalable, results in homogeneous mixing of transition metal cations, and additionally results in particles that with appropriate processing provide morphology tunability. Understanding the kinetics of the nucleation and particle growth during coprecipitation from a multicomponent blend solution is necessary for rational control of particle composition and morphology. In this talk we will demonstrate a combination of techniques to successfully obtain the in-situ particle size distribution and solution composition. The combined information was used to determine the reaction rate and mechanisms of particle nucleation and growth. The techniques developed in this study can also be applied to other multicomponent coprecipitation systems to guide their particle synthesis.

COLL 495

Colloidal semiconductor CdSe magic-size clusters with 415 nm bandgap

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The identification of non-bandgap electronic transitions of colloidal semiconductor magic-size clusters (MSCs) via optical absorption has been challenging, due to possible presence of other-bandgap ensembles in synthetic batches. Herein, we report one
example, CdSe MSC-415, referred to as the optical absorption peak position in nanometers of wavelength. For the CdSe MSC-415 ensembles reported, their syntheses were performed in aqueous or organic solutions, with phosphine/phosphine oxide, phosphinate, carboxylate, or amines as surface ligands. In addition to the bandgap absorption peak at 414 to 422 nm, another two absorption peaks in the range from 382 to 398 nm and from 352 to 365 nm have been often reported. For the two shorter-wavelength peaks, their absorbance is much weaker and they have been generally taken respectively as due to the secondary and third electronic transitions of MSC-415. For the origin of two commonly documented absorption peaks at ~381 and ~351 nm, we used our two-step approach to synthesize the MSCs. We show that the evolution of the two peaks does not synchronize with that of the ~415 nm peak and seems to be related to the disappearance of MSC-391 and MSC-361, respectively. Accordingly, these two peaks detected are probably not due to higher order electronic transitions in MSC-415. The present study suggests that it is necessary to re-evaluate previous experimental results and calls for efforts to develop advanced theoretical models to better comprehend the quantized energy levels of semiconductor MSCs.

COLL 496

Applying charge equilibration methods to CdSe quantum dots to gain atomistic insight into the magic-size phenomenon

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Semiconducting quantum dots (QDs) exhibit tunable size dependent properties, leading some to designate these materials as “artificial atoms”. Synthetic methods of CdSe QDs have been highly refined and typically involve one-pot seeding and growth, resulting in the generation of colloidal crystallites ranging in diameter from ~1nm to ~6nm and with size distributions as low as 10%. Several reports describe the observation of “magic size” QDs during the early stages of growth, characterized by a stepwise increase in QD size—as opposed to the typically-observed continuous growth of QD sizes. While postulated to result from QD structures of energetic stability, evidence of the nature of stable structures is limited in experiment by microscopy and in computational simulation by the sheer number of electrons present within even the smallest of QDs. This work highlights a new computational approach toward treatment of QD behavior that forgoes quantum mechanical (electronic state) information in lieu of computational speeds many orders of magnitude faster than ab initio methods. The modification of traditional charge equilibration (qEQ) methods to also account for the unique dielectric environment experienced by a QD during its synthesis (QD-qEQ) yields an approach that is fast and atomistic, providing rich information about the partial charge of each atom in the system at energetic equilibrium. When applied to a structure-set of 35,000+ unique wurtzite CdSe QDs with diameters ≤ 2.50 nm, energetic depressions are apparent at certain QD sizes, which agree generally with the sizes at which CdSe magic size QDs have been reported experimentally. Further, analysis of QD surface characteristics associated with such magic sizes yield surfaces made up of highly coordinated and relatively low energy
atoms, suggesting that the magic size phenomenon is due to a thermodynamic stability afforded by certain QD surface atom arrangements. The accuracy and versatility of QD-qEQ positions this method as a potential candidate for simulation of QD properties at much larger scales, an intractable problem with traditional computational methods.

COLL 497

Effects of branch morphology and crystallinity of Au-Co nanoparticles for enhanced oxygen evolution catalysis

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Au-CoOx hybrid nanoparticles have attracted a great deal of interest for oxygen evolution reaction (OER) catalysis in electrochemical water splitting due to their enhanced catalytic activity. However, the development of these electrocatalysts is limited by the lack of successful synthesis of Au-CoOx core-shell nanoparticles. Herein, we designed Au-Co branched nanoparticles by using an organic-phase seed mediated approach. We found that the 1D branch morphology and high crystallinity of the branched nanoparticles increase the charge transfer and improve the catalytic active sites for the oxygen evolution reaction. Importantly, these Au-Co branched nanoparticles show superior charge transfer and catalytic activity toward oxygen evolution reaction. This work opens a new avenue towards next-generation Au-Co based electrocatalysts for the oxygen evolution reaction.
Latent fingerprint development and imaging with NIR(980nm)-to-NIR(800nm) upconversion nanocrystals

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Many methods and protocols are available for latent fingerprint development and imaging. Yet, imaging become challenging when the background has complex patterns or is fluorescent. Fingerprints developed with NIR (800nm) emitting upconversion nanocrystals stand out, because the imaging technique strongly suppresses the background. This is due to the fact that most organic dyes and pigments found in printed materials have little or no absorbance in the NIR region and do not show any fluorescence upon 980 nm excitation. Aside from ‘zero’ background imaging, we demonstrate several additional advantages of using the 800nm emitting (48%Yb/2%Tm: β-NaYF₄) upconversion nanocrystals for latent fingerprint development. The advantages include: 1) the nanocrystals are capped with oleate, which helps in fingerprint selectivity; 2) 800 nm luminescent image can be captured in room light with the help of bandpass filters; and 3) high internal quantum yield of the NIR emitting upconversion nanocrystals (2.5% at 1.6 W/cm² power). Further, we evaluate the effect of the size of the nanocrystals on the quality of fingerprint development. The internal metrics, brightness, contrast, and resolution were used for fingerprint quality evaluation. Preliminary results
suggest that the larger nanocrystals (~240nm) exhibit improved brightness and contrast without compromising the resolution of the fingerprint compared to the smallest nanocrystals used (~70nm).

**COLL 499**

**Novel clustered state of colloidal dispersions: Transport properties of concentrated dispersions of particles with competing interactions validated against measurements of lysozyme with application to biopharmaceuticals**

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The "clustered state" of colloidal dispersions and the related intermediate-range microstructural ordering in Lysozyme protein solutions have been extensively explored experimentally, and explained theoretically based on a short-range attractive plus long-range repulsive (SALR) interaction potential. We scrutinize for the first time the applicability of semi-analytic theoretical methods predicting diffusion properties and the viscosity in isotropic particle suspensions to low-salinity Lysozyme protein solutions. The self-consistent Zerah-Hansen (ZH) scheme is used to describe the static structure factor, S(q), of Lysozyme solutions for different concentrations and temperatures obtained by small-angle neutron scattering. Samples belonging to the dispersed-fluid and random percolated phases are considered. The calculated S(q)'s are the input to our calculation schemes for the short-time hydrodynamic function H(q), and the zero-frequency viscosity. These schemes account for hydrodynamic interactions included on an approximate level. Theoretical predictions for H(q) as a function of the wavenumber q quantitatively agree with experimental results at small protein concentrations obtained using neutron-spin echo measurements. At higher concentrations, qualitative agreement is preserved although the experimental hydrodynamic functions are overestimated. We attribute the differences for larger concentrations to translational-rotational diffusion coupling induced by the shape and interaction anisotropy, and the patchiness of the Lysozyme particles, features not included in our globular particle model. The theoretical results for the viscosity are in semi-quantitative agreement with our experimental data even at larger concentrations. We demonstrate that semi-quantitative predictions of the diffusivity and viscosity of dispersions of globular proteins are possible given only the equilibrium structure factor of the solution. The hindered diffusion of the intermediate range ordered state is further explored by simulations and the extended application of this understanding to biopharmaceutical (monoclonal antibody) dispersions is explored.

**COLL 500**

**Strategies of optimizing CO₂-responsive assemblies by understanding their switching behaviors and feasibility in application**
CO$_2$-responsive interfacial-active materials have potentials in various applications, because of their ability to modify interfacial properties precisely and exquisitely during continuous operation. There are not only growing demands of developing versatile and cost-efficient chemicals and understanding their switching behavior, but also great interests in proving their feasibilities in applications. Herein, we present general strategies of constructing CO$_2$-responsive surfactant assemblies based on electrostatic attraction between amines and fatty acids on the interface, which allows easy fabrication, facile tunability, and possibility of scale-up. Interfacial activity and switching behavior were found to be readily adjusted as desired by selecting the types of amines and fatty acids, respectively. Dynamic IFT experiments not only revealed that switches upon CO$_2$ addition are rapid and significant, but also illustrated that responsive behaviors are not necessary to be the same in bulk and on the interface. These CO$_2$-responsive surfactant assemblies were successfully applied to enhance heavy oil recovery in northern Canada oil sands by finely controlling interfacial properties at different operation stages. This study highlighted the strategies of constructing CO$_2$-responsive assemblies in facile manners and controlling their switching behavior on the interface. The results from this study provide valuable guidelines on designing CO$_2$-responsive chemicals applications.
Polymer mediated interaction between colloids and their effect on thermodynamic properties of filled polymer melts and blends

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The polymer mediated (PM) interactions between colloids immersed in polymer melts, polymer blends, and rubber materials are studied by making use of the liquid state theory. A significance of the effect of attractive polymer-colloid and polymer-polymer interactions on the effective forces acting between colloids immersed in a polymer melt is shown to drastically depend on the colloid-to-polymer size ratio. For the case of colloids immersed in polymer blends we predict a novel mechanism of the PM interactions caused by non-uniformities in the local composition of the polymer blend induced by these colloids. This mechanism due to the compositional non-uniformity, specific to polymer blends, is shown to play a dominant role in the PM interactions. As a practical application of the developed approach, we study the polymer mediated coagulation and aggregation of the colloids immersed in the above host polymer systems. Further, we investigate the effect of colloidal particles on the phase separation in polymer blends. In addition, we discuss several practical examples showing how the effective interactions between colloids induced by polymers can be used to drive thermodynamic, mechanical, and electrical properties of selected polymer-colloid systems.

COLL 502

How do surfactants control the agglomeration of clathrate hydrates?

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Clathrate hydrates are nonstoichiometric compounds in which guest molecules are entrapped within a crystalline network of water cages. On the one hand, clathrate hydrates have promising applications in energy recovery and gas storage. On the other hand, high pressure and low temperature conditions in oil and gas carrying pipelines favor the formation of clathrate particles. The agglomeration of these clathrate particles leads to plugging of the pipelines posing adverse safety, economic, and environmental threats. Surfactants are widely used to prevent the aggregation of clathrate particles and their coalescence with water droplets. It is assumed that a large contact angle between the surfactant-covered clathrate and water is a key predictor of the anti-agglomerant performance of the surfactant. In this work we use molecular dynamic simulations to investigate the structure and dynamics of surfactant films at the clathrate-oil interface, and their impact on the contact angle and coalescence between water droplets and hydrate particles. In agreement with the experiments, simulations predict that the surfactant-covered clathrate-oil interfaces are oil wet but superhydrophobic to
water. We find that the water-contact angle determines the driving force for the coalescence. However, a large contact angle is not sufficient to predict good anti-agglomerant performance of a surfactant. We elucidate the effect of the length of the surfactant molecules, the density of the interfacial film, and then strength of binding of its molecules to the clathrate surface towards the coalescence and agglomeration of clathrate particles with water droplets in oil. Our analysis presents principles for the molecular engineering of effective clathrate anti-agglomerants.

COLL 503

Effects of antifreeze proteins and their hyperactive mutants on calcite crystallization

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Formation of inorganic salts (i.e., scale deposits) is a problem in industrial and domestic setting. To control scale deposits, chemical scale inhibitors are commonly used. Commercial antiscalcing agents include polyelectrolytes that dissociate potentially harmful phosphonates, carboxylates, and sulfonates anionic groups. Thus, it is imperative to identify highly efficient polymeric inhibitors to replace phosphonate inhibitors due to their environmental risks. Ice-binding proteins or antifreeze proteins (AFPs) from cold-adapted organisms can bind to specific ice surfaces, thereby inhibiting the nucleation and crystallization of ice. AFPs can also control the crystallization of some non-ice like compounds by interacting with the crystalline surfaces of these compounds. We correlate the charge and molecular properties of the polyelectrolytes with their efficiencies in inhibiting the scale crystal formation. A beetle AFP from Tenebrio molitor (TmAFP) having regular spaced charged residues on its surfaces is prepared and studied here. Calcium carbonate (CaCO₃) is a scalent of interest in this study. We investigate the effects of TmAFP and their mutants on the formation of CaCO₃. One TmAFP mutant (D4) was modified with aspartate residues interspersed at equidistance apart from each other. The second TmAFP mutant (N5) was modified by removing all negatively charged residues, aspartate and glutamate, and replacing them with asparagine. Results show that the presence of TmAFP inhibits the formation of CaCO₃, resulting much fewer CaCO₃ crystals. The effect is more pronounced in the mutants. By analyzing the charged residues on the surfaces of TmAFP and calcite surfaces, we propose that TmAFP may affect the formation of calcite via adsorption to the crystalline surfaces of CaCO₃. This study provides better understanding for scale control as well as new designs for green antiscalants.

COLL 504
Controllable fabrication of ultra-thin capsules encapsulated with smart nanogels for simple detection of lead(II) ions

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Lead, one of toxic heavy metals, possess serious consequences to the environment, human health and other living organisms. The ingestion of lead can cause damage to the central nervous system, dysfunction to the kidneys and immune system of human beings. Therefore, it is extremely necessary to efficiently detect and remove of lead(II) ions in water. Herein, we report the controllable-fabricated ultra-thin capsules encapsulated with smart nanogels for simple detection of lead(II) ions. The smart nanogels are made of poly(N-isopropylacrylamide-co-acryloylaminobenzo-18-crown-6) (PNB), and the capsules are made of calcium alginate. The monodisperse capsules are controllably fabricated with a co-extrusion minifluidic device. Due to the fast responsive volume phase transition and the high selectivity to lead(II) ions of the smart PNB nanogels, the PNB nanogels can recognize lead(II) ions and form stable positively charged B18C6Am/Pb^{2+} host-guest complexes isothermally as soon as lead(II) ions permeate through the capsules shell into core compartment. The electrostatic repulsion within the complexes will enhance the hydrophilicity of PNB nanogels and thus increase osmotic pressure inside the capsules, resulting in continuous permeation of lead(II) ions as well as water and the resultant swelling of capsules until reaching the osmotic balance. A simple glass device with scale is developed to study the isothermal Pb^{2+}-responsive swelling properties of capsules by measuring the change in outer diameter of capsules. Quantitative detection is achieved by the relation between the concentration of lead and volume swelling ratio of capsules. By this method, the detection of Pb^{2+} with concentration as low as 10^{-9} mol\cdot L^{-1} can be achieved. Such a smart capsule provides a simple method for detection of lead(II) ions and exhibits high potential for applications of different trace substances to protect environment and human health.

COLL 505

Rheological properties of hard-sphere suspensions in biaxial shear flow

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Densely packed particle suspensions exhibit interesting non-Newtonian rheological properties such as discontinuous shear thickening (DST) when a suspension above a critical particle volume fraction is subjected to a shear stress greater than a critical value. Such behavior arises from the build-up of frictional contact forces between particles greater than hydrodynamic forces such that the viscosity of the suspension
increases dramatically. Both experiments and simulation have shown that particle-particle and particle-medium interactions are important factors governing the critical volume fraction and shear stress. This talk presents recent biaxial shear experiments utilizing an orthogonal superposition technique on dense hard-sphere suspensions. We investigate commercially available glass microspheres and synthesized silica nanosphere suspensions with different particle surface chemistry and suspending medium. Our biaxial shear protocol is demonstrated to be a robust method on elucidating microstructural changes related with DST as well as providing guidance to shear thickening fluid applications.

**COLL 506**

Stabilization of nano-HMX suspensions with PVP to improve the milling process

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The focus of this work is to investigate the polymeric stabilization of cyclotetramethylene tetranitramine (HMX) suspensions using polyvinylpyrrolidone (PVP). The PVP adsorption on HMX surface was studied using zeta potential measurements, which revealed that the shorter PVP polymer chain (lesser molecular weight) adsorbed better than the longer one (greater molecular weight). This study also showed that the solvent dramatically affects the PVP adsorption. A turbidity test was conducted, showing that lower molecular weight PVP offers better stability. This stability is enhanced by increasing the ethanol concentration. The depletion mechanism was responsible for HMX stabilization with ethanol. Finally, a milling study was conducted to compare the HMX with and without a stabilization mechanism. This study indicated that PVP in 50% water/50% ethanol was able to stabilize HMX by depletion and reduce the size to 180 nm within 10 minutes of milling. Strong aggregation was observed for HMX milled in the absence of the stabilization mechanism. The stabilization techniques discussed in this study appeared to lead to a shorter processing time and a more efficient milling process when utilized. Under comparable milling conditions, a particle size of 180 nm could be achieved with stabilization compared to 500 nm without. Such a dramatic improvement of the milling process bodes well for future nanoHMX production, as well as that of similar materials.

**COLL 507**

Effect of electrolyte type and concentration on the electrokinetic behaviour of clay-polyelectrolyte dispersions

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Investigating the electrokinetic behaviour of clay suspensions is of prime importance in many industrial applications. In this study, the influence of the type and concentration of electrolytes on clay suspensions flocculated with anionic polyacrylamides has been investigated. These polyacrylamides differ in terms of charge density and molecular weights. The presence of electrolytes was found to induce profound impact on the flocculation behaviour of clay-polyacrylamide dispersions, analysed by means of floc size distribution tests. Introduction of electrolytes exhibited a significant increase in the average floc size of the flocculated clay dispersions. Electric double layer compression and mediated flocculation by metal cations were predicted as the principle mechanisms involved in the improvement of flocculation behaviour. Divalent electrolytes were more efficient in enhancing the flocculation behaviour of clay-anionic polyacrylamide suspensions than monovalent ones. Apart from electrolytes, polymer characteristics also affected flocculation behaviour. The molecular weight of anionic polyacrylamides greatly influenced the floc size distribution. High molecular weight polymer chains increased bridging opportunities with clay particles producing larger flocs. Overall, this study successfully determines the effect of electrolytes on the flocculation behaviour of clay-polyelectrolyte suspensions.

**Nanocellulose coatings on cellulose non-woven fabrics: High flux affinity membranes for water purification**

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Water re-use is increasing its significance due to the overall water shortage in many countries around the world. Membrane technologies are gaining more attention in water and wastewater treatment processes due to their reliable removal of contaminants without the production of harmful products. Increasing environmental awareness and demands for reusable and degradable products have driven the replacement of traditional membranes in water filtration systems, which are typically made of non-degradable and toxic materials, for membranes fabricated from renewable resources such as cellulose.

Previous studies of our group revealed the outstanding performance of nanocellulose and nanochitin as well as the potential of these materials as a next generation affinity membranes for water purification. The aim of the current study was the development of new nanocellulose and/or nanochitin based coatings on the surface of cellulose non-woven fabrics using cast coating as main technique. After coatings, water transport through the membranes was favoured and high flux performance was maintained, despite a slight decrease in the porous structure, due to the improvement of the wettability of the membranes, making them more hydrophilic. In addition, the membranes are designed for disposal by composting and their impact on environment, at end-of-life, will be evaluated through the study of its degradation in soil as well as its capacity as a fertilizer.
These new coating formulations based on green nanotechnology in the form of nanotextured membranes will be more efficient, cost effective, and environment friendly than currently available membranes or adsorbents; providing sustainable and upscaleable membrane processes and their integration into water recycling from industrial effluents.

**COLL 509**

**Garment-integrated thermoelectric devices**

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Body-mounted thermoelectric devices are a promising energy source for powering wearable electronic devices. However, known iterations of body-mounted thermopiles have large form factors, contain expensive materials with low elemental abundance, and quickly reach thermal equilibrium with a human body, meaning that thermoelectric power can only be generated over a short period of wear. We will discuss our lab’s efforts in using reactive vapor coating to create unique fabric- and fiber-based electronics and describe a high-performing wearable thermopile created in our lab. A garment-integrated, all-fabric thermoelectric generator was created by coating commercial cotton fabrics with persistently p-doped poly(3,4-ethylenedioxythiophene) (PEDOT-Cl) using a solvent-free, reactive vapor deposition method. Simple, two-leg thermoelectric devices created out of these coated fabrics continuously generate upwards of 20 mV during wear. We show that reactive vapor deposition is particularly important in creating mechanically-rugged conductive fabric coatings that yield notably-high thermoelectric power factors at low temperature differentials, as compared to solution-processed counterparts. We will also discuss unique variables that affect the performance of wearable, fabric-based thermoelectric generators, such as sweat level and skin surface biochemistry.

**COLL 510**

**Electrochemical properties of 3-dimensional flexible substrates with iridium oxide nanoparticles for use as a supercapacitor**

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The Army seeks to address the power and energy (P&E) needs of the Soldier by investigating commercial fabric materials as electrodes, enabling advances for energy
storage on fabric electrode platforms with minimal burden for the Soldier in the field. In this work, we report methods to deposit iridium oxide nanoparticles (IrOx NPs) onto flexible light-weight materials for charge storage and examine electrochemical properties on the electrodes. In this work, IrOx NPs were electrodeposited onto commercially available flexible surfaces of both knit and nonwoven cotton, and nonwoven carbon-based (carbon nanotubes and graphene) textile substrates. The flexible electrode materials were fabricated by reducing graphene oxide onto cotton fabric or binding carbon nanotubes/graphene into a standalone platform. Iridium oxide was electrodeposited as NPs of less than 2 nm in size to serve as a redox active component to increase energy capacitance. Two nanoparticle deposition processes were investigated as well as the electrochemical properties of the integrated fibrous electrode configuration. Cyclic voltammetry was used to measure electron transfer properties and capacitance. Additional measurements were conducted to determine electrical resistance, surface area, energy and power densities, and charge/discharge rates (GCD). Results show a specific capacitance value increase over all three base fabric materials up to 2,747 percent. After electrodepositing IrOx NPs onto the textile electrodes, the active sites available for charge storage increased between 59 and 90 percent. The increase in both the specific capacitance values and total active sites indicate that IrOx NPs greatly enhance the charge storage capability of fabric materials. The integrated flexible electrodes were shown to be electrochemically stable over 1,000 GCD cycles. This research will advance fundamental understanding of relationships between high surface area electrodes and the use of redox reactive nanoparticles on charge storage mechanisms.

COLL 511

Textile functionalization by porous protein crystal conjugation and guest molecule loading

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Protein crystals are versatile nanostructured materials that can be readily engineered for applications in nanomedicine and nanobiotechnology. Despite their versatility, the minute size of individual protein crystals presents challenges for macroscale applications. One way to overcome this limitation is by immobilizing protein crystals onto larger substrates. Cotton is composed primarily of cellulose, the most common natural fiber in the world, and is routinely used in numerous material applications including textiles, explosives, paper, and bookbinding. Here, two types of protein crystals (hen egg white lysozyme and a porous crystal composed of an isoprenoid binding protein from C. jejuni) were conjugated to the cellulosic substrate of cotton fabric using a 1,1'-carbonyldiimidazole/aldehyde mediated coupling protocol. The efficacy of this attachment was assessed via accelerated laundering and quantified by fluorescence
imaging. The ability to load guest molecules of varying sizes into the scaffold structure of the conjugated protein crystals was also assessed. This work demonstrates the potential to create multifunctional textiles by incorporating diverse protein crystal scaffolds which can be infused with a multiplicity of useful guest molecules.

Porous protein crystals (green) attached to cotton and loading with guest enzymes (red)

COLL 512

Inorganic nanocoating technology for functional textile

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Functional textiles have seen a growing industrial interest over the last few years. Their development is driven by a wide range of applications including healthcare, wearable electronics, bio/chemical sensing, piezoelectric actuation, energy harvesting and storage, sports clothing, drug delivery for skin care, thermal insulation, and military applications such as electromagnetic interference shielding. In general, a functional textile needs to demonstrate specific properties including specific functionality, general
durability and health/environmental safety of the products. While the functionality component has seen significant advancement, the growth of this market is hindered by the limitations and costs inherent to the functionalization processes, the short durability of currently available products, and the subsequent environmental concerns. In my upcoming talk, I will introduce a new inorganic nanocoating process named “Thermal Creascoating”, based on thermal growth of inorganic nanoparticles on a variety of textiles. This is a chemical-free process that only requires the use of a precursor ion. As a result, the same process can theoretically be used to grow any type of metal, metal oxide and metalloid nanoparticles on any fibrous material. During the impregnation step of crescoating, the precursor ions not only adsorb to the surface of the fibers but also undergo subsurface diffusion to penetrate inside the bulk material of the fibers. As a result, nanoparticles grow not only on the surface but also throughout the fibers to form stable and functional nanocomposites, thus increasing the functional surface area while preventing the release of the nanoparticles. The importance of nanoparticles lies in their ability to confer multiple functionalities including antimicrobial, sorption, optical, catalytic and conductive properties, and the remarkable enhancement of these functionalities due to increased surface-to-volume ratio and high surface energy. Some examples of creascoated materials and their functionality will be presented, as well as some perspectives in the field.

COLL 513

Directed evolution of tandem repeat protein fibers

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Design and expression strategies for the production of repetitive proteins (e.g., silk, SRT, elastin, collagen) that comprise one or more tandem copies of a single unit have been an interested for the last couple of decades. Tandem repetition intrinsically promotes stability through the periodic recurrence of favorable interactions; hence modular reuse allows for a stepwise increase in functionality in the biomaterial design. However, the design of highly repetitive sequences for structural proteins present challenges for protein engineering. For example, the construction of the synthetic genes encoding them can fail or generate nonspecific products. Recently, we developed a novel technique (see Figure) combining ultrafast laser-probing spectroscopy and protein in-vivo assays to study directed evolution of tandem repeat proteins. Our technique enables screening of a large library of structural polypeptide sequences for protein assembly in hours, a feat that would be impossible to achieve with existing screening tools such as fluorescence, immunostaining, or functional assays. Using this technique we created tandem repeat protein fibers. These materials can be shaped into various geometries such as fibers, colloids, and thin films. Moreover, their molecular structure provides a rich architecture that can micro-phase-separate to form periodic nanostructures (e.g., lamellar and cylindrical repeating phases). In this talk, we focus on directed evolution of protein-based programmable fibers, with applications to textile.
Directed Evolution of Tandem Repeat Protein Fibers

COLL 514

Colloidal chemistry of NFC based sustainable textile dyeing technology and factors affecting dye performance

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Fibrillated Nanocellulose (NFC) is a non-toxic, one dimensional (1D) nanomaterial engineered from abundantly found cellulose sources. NFC is produced in the form of a stable thixotropic hydrogel. The hydroxyl groups in the NFC matrix provide efficient reactive sites for chemical reactions, modifications, and post-treatments. Due to such chemical and structural significances, NFC becomes a perfect alternative for creating
green chemistry to the textile coatings including dyeing technologies which substantially reduce consumption of water and release of hazardous effluents to the environment. NFC based sustainable textile dyeing technology involves reacting textile dyes with NFC and forming a NFC-dye hydrogel. The dye fixed to nanocellulose is converted to a fibrous pigment (on the nanoscale). NFC ensures the permanent retention of the dye via a combination of strong hydrogen bonds and fibrous (entanglements) mechanism of adhesion. NFC based sustainable textile dyeing technology promises more than 80% dye fixation, excellent dye performance, and colorfastness. This technology consumes ten times less water and dye auxiliaries compared to the exhaust dyeing method.

Soluble sugars presence in NFC hydrogel plays a pivotal role in achieving a high level of dye fixation. Chemical analysis of soluble sugars reactivity in NFC dye dispersions has shown that soluble sugars favor dye fixation through the chemical crosslinking post-treatments. Developed post-treatment is involved using polycarboxylic acids as the crosslinking agent. Polycarboxylic acids can make ester crosslinks between fabric cellulose fibers and NFC matrixes that carry covalently bonded dye molecules. Hence, chemical crosslinks can fix NFC-pigment permanently to the fabric surface. Thus, dye performances (fixation, colorfastness, and color retention) can be further enhanced, and dye discharge during the washing process can be significantly reduced.
Figure 1: SEM analysis of NFC- reactive blue dye coating retention on 100% woven cotton after 10 laundry cycles

COLL 515

Fabric modification with nanocellulosic fibers as functional carriers

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This research focuses on efficient, universal, and environmentally friendly method of fabric modification (such as dyeing, finishing, functionalization) using nanocellulosic fibers (NCF). From a practical point of view our process has been designed to be readily scalable, transferable between different fabrics and to consist of small number of
technological steps. In essence, we target fabrication method where chemical processes and fabric modification are separated in space and time thus the conditions for the chemical reactions are no longer restrained by substrate and chemical proficiency of the operator. In our design, first, the chemical reactions are carried out to modify NCF using the powerful chemical arsenal developed for cellulose based materials. Then, the modification of fabric is a straightforward and quite universal process, where modified NCF are deposited from water on fabric using current manufacturing tools such as padding, spraying and printing. In our initial study we have modified NCF with attachment of reactive dye molecules to form a colored dyed-NCF solution. Different concentrations of dyed-NFC have been used to modify cotton, nylon and PET fabrics. It was observed that the color of fabrics is quite homogenous for each concentration of dyed-NCF. However, the stiffness of fabrics is increased after the addition of NCF, which can be attributed to the addition of the high-modulus NC fibers to fabrics as well as increased friction between interwoven fibers. To resolve this challenge we have used molecular bottlebrush reactive copolymer additives such as poly(Oligo Ethylene Glycol methyl ether Methacrylate- Glycidyl Methacrylate- Lauryl Methacrylate) and poly(Oligo Ethylene Glycol methyl ether Methacrylate- Glycidyl Methacrylate). Also in colorfastness test it was observed that both copolymers have a positive effect on color stability of the modified with NCF fabrics.

COLL 516

Fluorinated quantum dots

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Fluorination of surfaces is an effective strategy for inhibiting corrosion and blocking redox reactions, but the toxicity of fluorinated compounds mandates that their concentrations be minimized. Here we discuss the permeabilities of self-assembled monolayers of fluorinated aliphatic compounds on semiconductor quantum dots, and their use as CO$_2$ concentrating layers to enhance the photocatalytic activity of the particles for CO$_2$ reduction.

COLL 517

What calorimetry can teach us about quantum dots: A tale of ITC

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The surface chemistry of semiconductor nanocrystal (NC) quantum dots (QDs) is intimately connected to their photophysics. Synthetic conditions and solubility requirements often demand that surface ligands be post-synthetically modified in order to tailor QD properties to an intended application. In the Keene lab, we have deployed isothermal titration calorimetry (ITC) as a dynamic technique to gain understanding of
ligand exchange reactions on QDs as they occur. ITC is a technique that has long been utilized in biochemistry to study the thermodynamics of interactions between two macromolecules such as enzyme-protein binding events, and yields a full thermodynamic sweep with a single experiment. We have studied two model ligand exchange reactions on oleate-ligated CdSe QDs that are both established and relevant, dodecylphosphonic acid and pyridine, to demonstrate the effectiveness and utility of ITC in the field of QDs. Here I present the results of these ligand exchange ITC studies and provide information including enthalpy, reaction stoichiometry, equilibrium constant, Gibbs free energy, and entropy for the reactions. In the example of dodecylphosphonic acid, coupling the thermodynamic data with external post-synthetic measurements such as X-ray diffraction, thermogravimetric analysis, and transmission electron microscopy allows us to make insights into the modification of not only the surface ligands, but also the surface and near-surface atoms of the QD crystal during the ligand exchange reaction. For the first time, we report the experimental measurement of energy absorbed by rearrangement of surface atoms on QDs as a result of stronger-binding ligand molecules. Conversely, study of the weaker-binding pyridine demonstrates how the raw isotherm from ITC can be interpreted along with the thermodynamic data to develop a more efficient, less wasteful, and faster ligand exchange protocol. We also investigate the role of solvent selection in this ligand exchange reaction. These studies highlight the established technique of ITC as an emerging opportunity when applied to nanomaterials to gain a deeper understanding of the processes that are so vital to the form and function of colloidal semiconductor NCs.

COLL 518

Design of histone-mimic nanoparticles for DNA and RNA compaction using molecular modeling

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The design of ligand functionalized inorganic nanoparticles (NPs) that can induce specific structural transitions in nucleic acids (NA) is important for nanotechnology applications including gene delivery and nanoelectronics. However, comprehensive understanding of ligand design principles lies in the cost associated with synthesizing and characterizing diverse ligand chemistries and ability to carefully assess the structural integrity of biomolecules upon interactions with NPs. It is known that the interaction of nucleic acids and nanoparticles may be tuned through changes in nanoparticle size, charge, polarity, or shape. However, the factors that affect structural transitions are not fully understood. We performed atomistic molecular dynamics simulations of the binding of nucleic acids to monolayer-protected gold nanoparticles to elucidate structural changes that take place for nanoparticles and DNA upon binding. Results from these simulations were analyzed to determine modes of DNA and RNA bending with nanoparticles. Our simulations show that highly charged nanoparticles cause DNA to bend with little damage to the helix structure, similar to DNA in the
nucleosome. Nanoparticle shape as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. Low salt concentrations and high nanoparticle charge cause greater disruptions to DNA structure. We find that the roll parameter is the most important base-pair parameter for DNA bending. Requirements for bending differed significantly between DNA and dsRNA. The degree of DNA bending is controlled by the charge of the NPs, but ligand flexibility played a more significant role in dsRNA bending. These results allowed us to determine the training data for machine learning algorithms and design a novel ligands capable of controlled wrapping of NA around NP. We have shown that the designer gold NPs are capable of wrapping NAs with fine control of binding strength through NP charge and ligand stiffness. These findings are useful for designing gene delivery systems with enhanced biocompatibility and selectivity.

COLL 519

Spatially controlled bioorthogonal catalysis for imaging and drug delivery

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Bioorthogonal transformation of prodrugs and profluorophores using transition metal catalysts (TMC) offers a promising strategy for imaging and therapeutic applications. However, maintaining activity and controlling the localization of TMCs make their use in biomedical applications challenging. Here we report the engineering of nanoparticles of gold nanoparticles (AuNPs) with encapsulated TMCs (nanozymes) to provide specific intra- and extracellular localization. We used membrane-penetrating cationic nanoparticles for catalysis inside and ‘stealth’ zwitterionic particles to limit catalysis to outside of mammalian cells. Specific localization of nanozyme activity was demonstrated through profluorophore activation. Therapeutic efficacy was demonstrated through intra- and extracellular activation of a prodrug. The ability to control nanozyme localization was further shown by targeting biofilms in a complex bio-system using a co-culture model. We designed pH-switchable nanozymes that effectively localize in the acidic microenvironment of biofilms. These nanozymes generate imaging agents through bioorthogonal activation of profluorophores inside biofilms demonstrating potential for early detection of biofilm-associated infections. Taken together, these studies demonstrate a new level of spatial control for TMC-mediated bioorthogonal catalysis for diagnostic and therapeutic purposes.
First, we discuss our modeling of binary systems of nanoparticles (NPs) which self-assemble at liquid surfaces. Our modeling reveals that NPs-liquid coupling energies form about 40% of the total lattice energy, which means that this coupling largely controls the types of NP-superlattices formed. We explain why different superlattices form and show why similar solvents can provide very different NPs self-assembly conditions. Next, we present our modeling of supercharged NPs that self-assemble in bulk solvents, and clarify the conditions under which different superionic lattices form.
Self-assembly of nanoparticles at liquid surfaces

Unveiling the surface chemistry of colloidal NaPnE$_2$ nanocrystals (Pn = Sb, Bi; E = S, Se)

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Many technologically relevant semiconductors contain toxic, highly regulated elements (Cd, Pb, As), or relatively scarce and poorly distributed elements (In, Li). In contrast, alkali-based APnE$_2$ semiconductors are made of biocompatible or relatively abundant elements (A = Na, K; Pn = Sb, Bi; E = S, Se). These ternary semiconductors adopt a rock salt structure, where the chalcogenide (E) forms an fcc lattice, and a mixture of monovalent/trivalent (A/Pn) cations occupies the octahedral holes. Along with the presence of polarizable lone s$^2$ electrons on Pn, this leads to efficient phonon scattering, which is ideal for thermoelectrics. APnE$_2$ semiconductors are also predicted to be defect
tolerant photovoltaics, much like halide perovskites, where point defects are unlikely to result in mid gap or trap states. We have successfully synthesized colloidal NaBiS$_2$ nanocrystals from commercially available precursors (J. Am. Chem. Soc. 2018, 140, 3736–3742). Just as the formation mechanism and phase evolution of ternary and more complex nanocrystals differ substantially from those of unary (elemental) or binary nanocrystals, the organic-inorganic interfacial chemistry of multinary nanocrystals is inherently more complex and unique. We use IR, NMR, and XPS to identify and quantify the native ligands present on the surface of colloidal NaPnE$_2$ nanocrystals. These include negatively charged X-type (carboxylate) and neutral L-type (primary amine) ligands, bound ion pairs or neutral acceptor Z-type ligands (NaX, BiX$_3$), and additional neutral L-type ligands such as thioamides, amidines, and thioethers formed during synthesis. Finally, we observe that smaller NaBiS$_2$ nanocrystals are much more stable to oxidation. The surface of these rock salt materials becomes more cation rich with decreasing particle size. Because both X and L type ligands preferentially binds cations, it makes sense that smaller particles containing mostly cation-only (111) facets are better passivated, and thus are more stable against surface oxidation. We also explore ligand exchange of the native ligands with dithiols (DHLA) and trithiols, under thermal and photochemical conditions, in order to produce water soluble NaPnE$_2$ nanocrystals. We hope this work will help unlock a new class of low cost and environmentally friendly ternary semiconductor nanocrystals for energy conversion.

**COLL 522**

**Structure and collective dynamics of boehmite-oriented aggregation**

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Although orientation-dependent forces governing crystallization by particle attachment have been reported, their scaling with particle anisotropy and solution chemistry remains unknown. Accordingly, the collective dynamics of systems exhibiting oriented attachment remain difficult to predict, particularly for non-spherical particles. In this context, we investigated the structure and dynamics of boehmite aggregation as a function of solution pH and ionic strength. Cryogenic transmission electron microscopy showed that boehmite platelets assemble by oriented attachment on (010) planes. The coagulation rate constants obtained from dynamic light scattering span both the reaction-limited and diffusion-limited regimes. We use simple scaling arguments, calculations of stability ratios, and rotational/translational diffusivities of irregular particle shapes to rationalize the effects of orientation on the early stages of aggregation. Using Monte Carlo simulations, we found that a nanoscale geometric parameter, namely the contact area between two attaching platelets, has a determining impact on the emerging macroscale aggregates and explains their unusually high fractal dimensions.
Enhancement of anaerobic digestion sludge dewatering performance using \textit{in-situ} crystallization in combination with cationic organic polymers flocculation

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Anaerobic digestion (AD) has been widely used in sludge treatment for biogas recovery, organic fraction stabilization and sludge reduction. However, after AD, sludge filterability is extremely deteriorated due to the release of biopolymers and the formation of fine particles. AD sludge is generally rich in nutrients, mainly ammonium nitrogen and phosphates, resulting from biopolymer degradation. We designed a conditioning process that combined the \textit{in-situ} crystallization of magnesium ammonium phosphate (MAP) as a skeleton builder with organic polymer flocculation. We show that crystallized MAP can bind with extracellular polymeric substance fractions to increase sludge floc density. The molecular structure and electrical charge of organic polymers importantly influence sludge particle flocculation and aggregation. We found that cationic polyacrylamides form flocs that aggregate with branching structures that are characterized by a larger size and a more compact structure. Simultaneous crystallization and flocculation produced by a magnesium–organic polymer gel improved AD dewaterability more than the separate addition of magnesium ions and organic polymers. The method of sludge conditioning that we propose was tested by extensive use in different AD sludge conditioning protocols. It reduces the ammonium nitrogen load in AD liquor and increases the suitability of the biosolids for use as land fertilizer.
Fusion is critically important process in alive and not alive nature. Fusion of the membranes is critical for morphogenesis, proliferation, regeneration process of the tissue, genetic manipulation of cells. Fusion of the organic and inorganic particles is essential part of the printing devices (3D printing fusion). There are several ways to control fusion, via utilizing the electrical field (electrofusion), electromagnetic field (optical fusion). Selected fusion is realized using the optical tweezers.

The chemical fusion of the soft matter under mechanical stirring in aqueous buffer is presented here. The difference in fractal growing is shown for the polymer microcapsules different by shape. The main tendency in particles fusion had been explained by strong hydrophobic interaction and screened electrostatic repulsion by salt. The mechanical stirring facilitates the microcapsules fusion and growth of the well-organized fractals. The spherical microcapsules (4 µm in diameter) form the colloidosome (Figure 1 A) while cubic shaped microcapsules of similar dimension forms cuboid like structures (Figure 1 B). The variation of the applied mechanical stirring (rate, direction, frequency) will potentially lead to the building of the programmable (controllable) microstructures. The obtained results are important for the tissue engineering, for instance, mimicking of the tissue by soft matter (such as blood clumping) as well as fusion printing of the soft matter.

Confocal imaging of the fusion of the spherical microcapsules to colloidosomes (A) and cubic to cuboid like structures (B) under the mechanical stirring.
Entry, bridging and spreading of n-hexane at the air/zwitterionic surfactant solution interface in presence of salts with respect to foamability and foam stability

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The behavior of oil droplet (i.e. n-hexane) at the air-water interface of the aqueous zwitterionic surfactant, N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS) was investigated. The oil droplets are usually employed as effective antifoam agents. The stability of foams is heavily dependent on the entry, bridging and spreading of the oil droplet at the lamellae and Plateau borders within the foam network. Thus, the stability of foam in presence of salt (NaCl, CaCl$_2$, and AlCl$_3$) was analyzed with respect to time. The droplet size varied with surfactant and salt concentrations. We discussed the feasibility of oil droplet to enter the interface by measuring the surface and interfacial tensions. The entry of oil droplet follows with the ‘bridging’ process, which involves entering of oil in both surfaces of lamellae and the Plateau borders which forms an unstable bridge across the film. Several forces tend to act to impart the stability to the foam films. The spreading of an oil droplet in the lamellar region also leads to a Marangoni effect.

In the present work entering (E), spreading (S), and bridging (B) coefficients were investigated to study the stability of foams in the presence of oil. The presence of oil decreased the foam volume and reduced its stability. These coefficients decreased with increasing salt concentration. Positive values of the spreading and bridging coefficients show that n-hexane has a destabilizing effect on foam. Low stability of the irregular oil–water–air films may impart a destabilizing effect on the foams (Figure). The effectiveness of the counterions in reducing the foam stability followed the sequence: Al$^{3+}$ > Ca$^{2+}$ > Na$^+$. 
Minute oil droplets present in the Plateau borders of a foam film.

**COLL 526**

**Synthesis of magnetically responsive Janus particles using biodegradable natural chemicals for functional magnetic emulsions**

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A magnetically responsive Janus (**Janus-M**) particle was designed and synthesized by sequential adsorption of hydrophobic ethyl cellulose (EC) and hydrophilic carboxymethyl cellulose (CMC) on a magnetic iron oxide nano particle. A Quartz Crystal Microbalance with Dissipation (**QCM-D**) instrument was used to evaluate and quantify the adsorption of EC and CMC on the iron oxide surfaces. The adsorption of EC and CMC on magnetic
nanoparticles was confirmed by zeta potential measurement, thermal gravity analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). Field Emission Scanning Electron Microscopy (FE-SEM) images revealed a good dispersion of Janus-M particles in both aqueous phase and organic phase. The coalescence time measurement and the crumpling behavior of particles-stabilized droplets along with the measurements of interfacial pressure-area isotherms demonstrated stronger interfacial activities of Janus-M particles and a stiffer interface adsorbed with Janus-M particles as compared with the interfaces stabilized by conventional interfacially active particles of uniform surface properties. The Janus-M particles were shown to be capable of stabilizing multiple oil-in-water emulsions while the microscopy images confirmed successful stabilization of emulsion droplets tagged by Janus-M particles. The magnetically responsive Pickering emulsions stabilized by Janus-M particles have potential applications in food science, drug delivery, biomedical technology, synthesis of functional nanomaterials, oil removal in environmental technology and oil production in petroleum industry.

COLL 527

Reversible sol-gel phase-changing electro-responsive smart particles-dispersed colloidal suspensions

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The electro-responsive particles-dispersed smart colloidal suspensions have reversible solid-like (gel) and liquid-like (sol) phase change properties and have gained great attention for various potential applications in actuators, wearable devices, medical haptic devices, aerospace, and electronic devices due to their controllable and reversible viscous behavior. However, they are still limited to apply in industries owing to the lack of knowledge for manufacturing and implementation of their functions. If methodologies for manufacturing of the electro-responsive smart materials are properly established, the smart colloidal suspensions are expected to be utilized in industrial fields more commonly. Herein, we offer the design method of the electro-responsive smart particles inspired by the electrophoresis separation of biomolecules. In order to imitate a biomolecule, the nitrile groups of a polyacrylonitrile (PAN) particle and alkylamine-length adjusted oligoamines such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and tris-(2-aminoethyl)amine (TAEA) were combined respectively by coupling reaction. The modified PAN particles with a short oligoamine present an electro-aligning behavior due to the enhanced dielectric property, while the modified PAN particles with a long oligoamine show an electro-migrating behavior owing to the improved electrophoretic force, as we expected. Our results have demonstrated that the introduction of the length-adjusted oligoamine groups onto the surface of the electro-responsive smart particles can improve both the electro-alignment and -migration by
controlling the electrophoretic effects and the dielectric properties. To our best knowledge, this is the first time that the electro-migrated smart colloidal suspensions are controllably obtained. Thus, we believe that our invention will boost the actual application of electro-responsive smart suspensions in various industries.

Control of viscosity in actuators using electro-responsive smart suspension

COLL 528

**Improving BFFT of waterborne polyurethane coating by building encapsulated polyisocyanate emulsion with hydrophobic inter-facial agent**

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In the transformation progress from solvent-based to waterborne of two components polyurethane coating based on the –NCO group, the problem of bubbles occurs quite common. The main reason is that traditional waterborne two components polyurethane coating system cannot effectively inhibit the side reaction between polyisocyanate in curing hardener and water. The difficulty to avoid the microbubble formed by the reaction of polyisocyanate with water in the process of film forming severely degrades the appearance and performance of the coating film. Herein, a novel hydrophobic network encapsulated inter-facial agent is added to the curing hardener, which physically separates the polyisocyanate emulsion from water. This achieves to reduce the contact between water and polyisocyanate, to suppress effectively on the side reaction between polyisocyanate and water, to increase the BFFT (bubble free film thickness) in the film forming process of the waterborne two components polyurethane
coating, and to improve application performance and the appearance of coating film. The influence of different amounts of hydrophobic network-coated interfacial agent on the performance were studied. The bubble-free film thickness index was investigated by optical microscopy, which guides the determination of the optimal amount of addition. Through this strategy, the bubble free film thickness of the waterborne two component polyurethane coating can be increased to about 1.5 times. The increased the broadness of application window is achievable. It provides a technical solution for the large-scale industrialization of waterborne polyurethane coating and the complete replacement of solvent polyurethane coating.

COLL 529

Structure-property relationship of commercial surfactants and bilgewater emulsions stability

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The presence of surfactants in bilgewater, or shipboard wastewater comprised of oils, lubricants and cleaning products, generates thermodynamically stable oil-in-water emulsions that are difficult to separate. Advanced treatment techniques are often employed to ensure compliance with the environmental discharge regulation that bilgewater must contain less than 15 ppm of oil. Due to micelle formation, surfactant behavior is key to understanding bilgewater emulsion formation and treatment. Therefore, a fundamental understanding of surfactants found in bilgewater has potential to lead to new treatments and improved prevention of bilgewater emulsions. Surfactant behavior is typically studied in clean systems where the concentration and molecular structure of the surfactant can be meticulously controlled. While these model systems have provided a foundational understanding of surfactants, their applicability to real-world systems such as bilgewater emulsions is often limited. In this work, we apply classical surfactant characterization techniques to eight commercial off-the-shelf (COTS) emulsifiers commonly used on armed forces vessels. The main components of each product were identified using nuclear magnetic resonance spectroscopy (NMR), liquid chromatography–mass spectrometry (LC-MS) and gas chromatography–mass spectrometry (GC-MS). The critical micelle concentration (CMC) of the pure mixtures was also determined. The detailed characterization of the COTS emulsifiers was complemented by conventional stability studies and interfacial tension measurements of prepared bilgewater emulsions. The role of environmental conditions (temperature, pH, salinity, etc.) on the stability of emulsions formed by COTS emulsifiers will be discussed, as well as implications for improved bilgewater treatment.

COLL 530
Multicomponent self-assembled gels: Compositional effects on rheological and tribological responses

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Polymers that form microgels are used in a wide range of applications from coatings, drug-delivery to personal care products. For the latter function, these polymers are also used in oil/water emulsions wherein the polymer is part of the continuous phase. In the emulsification process, phospholipids can replace traditional surfactants to prevent skin irritation and provide biocompatibility by forming a lamellar structure akin to the skin. In this study, we investigate how the type of microgel forming polymer (hydrophobically modified polyacrylic acid lightly crosslinked (HMPA) versus hydrophilic polyacrylic acid highly crosslinked (PA)) behave in an aqueous medium by themselves and in an emulsion in the presence of hydrogenated phosphatidylcholine phospholipids with different oil content. We examine the effect of composition on the rheological and tribological characteristics. For rheology, we examine their behavior in the linear and non-linear regime using small strain amplitude as well as large amplitude oscillatory shear (LAOS) experiments. We observe all systems to be gels with the elastic modulus ($G'$) dominating and frequency independent, and to exhibit yield stress. Systems containing HMPA show lower yield stresses and moduli than systems with PA, due to the difference in the crosslinking density. However, systems containing HMPA form a more interconnected network in an emulsion than in an aqueous environment due to hydrophobic interactions between the polymer and the phospholipids. Lissajous-Bowditch plots obtained to get information about microstructural transition under large deformation show that the emulsions with their 3-D bubbles can resist greater deformations with less increase in the viscous dissipation when compared to a gel. For tribology experiments we use a ball-on-disk configuration to obtain friction curves in a range of entrainment speeds using different substrates to mimic the skin surface (PDMS and Bioskin™). We find friction coefficients to be dictated by hydrophobicity of the substrate and polymer used at lower entrainment speeds, by substrate roughness at intermediate entrainment speeds, and by breakdown of the oil phase in the high entrainment regime. These results, taken together provide physical insights to tune and control the bulk rheological and surface frictional behavior of these microgel systems.

COLL 531

Combined supramolecular and mesoscale modelling of liquid–liquid extraction of rare earth salts

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We develop a minimal model of weak aggregation in water in the case of neutral extractant in a Winsor II regime, i.e. dispersed microemulsions in thermodynamic
equilibrium with concentrated brine. All the terms involved in the free energy associated with the transfer of ions from a concentrated aqueous to an organized organic phase have been estimated: supramolecular effects, bulk terms, extractant film bending and electric polarisation terms. This allows the rationalization of the paradoxical observation of apparent stoichiometry: “constant” associated with the phase transfer that varies with the nature of the solvent and the bending properties of the surfactant. The extractant film is characterized by its spontaneous packing parameter (of the order of 4) and its intrinsic rigidity of the order of 6.25 kJ mol$^{-1}$ (2.5 k$_B$T). This multi-scale study combining supramolecular chemistry and mesoscale modelling approach allows a large reduction of the number of parallel apparent equilibria currently used for dimensioning extraction devices. Prediction power versus variations of water activity and temperature is in reasonable agreement with observations made in typical pilot cascades.

**COLL 532**

**Studies of caffeine interactions with cations and osmolytes**

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Caffeine interactions with cations and osmolytes are investigated by a combination of thermodynamic and spectroscopic approaches. Effects of a series of chloride salts and osmolytes on the thermodynamics of caffeine partitioning between aqueous and cyclohexane are studied by using UV-vis spectroscopy. Standard Gibbs free energy for caffeine transfer is measured as a function of cation and osmolyte concentration and solution temperature. Standard enthalpy and entropy for caffeine partitioning in the presence of chloride salts and osmolytes are obtained. On the other hand, $^1$H and $^{13}$C NMR and ATR-FTIR spectroscopy are employed to determine how cations and osmolytes interact with caffeine. The spectroscopic experiments complement the thermodynamic measurements to illustrate the specific interactions of cations and osmolytes with caffeine molecule in solution.

**COLL 533**

**Mineralization in balanced salt solutions**

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Balanced salt solutions are widely used to maintain pH and tonicity of cells in culture for the manufacture of biopharmaceuticals. Commercial-scale manufacture of phosphate buffered balanced salt solutions that contain sodium, potassium, magnesium and calcium as supporting ions present a challenge for two reasons. First, the solution components can react to form insoluble precipitates. Second, precipitation is often unpredictable and therefore difficult to prevent.
This work focused on evaluation of a predictive model for pH values in phosphate buffered solutions with supporting electrolytes. In addition, the model was used to predict the conditions that lead to precipitation. Experimental measurements of solution pH and calcium ion activity in this system, were compared to model predictions for calcium phosphate mineralization. Based on the model, hydroxyapatite (Ca$_5$(PO$_4$)$_3$(OH) or HAP was predicted to precipitate under equilibrium conditions. However, the precipitate has been characterized as (Ca$_8$H$_2$(PO$_4$)$_6$·5H$_2$O), octacalcium phosphate (OCP), by using a combination of analytical techniques. Precipitated crystals of OCP remained stable even after being aged in the balanced salt solution. The results and practical application of a predictive model for avoidance of precipitation in phosphate buffered balanced salt solutions are discussed.

**COLL 534**

**Effect of electrolyte type and concentration on the electrokinetic behaviour of clay-polyelectrolyte dispersions**

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Investigating the electrokinetic behaviour of clay suspensions is of prime importance in many industrial applications. In this study, the influence of the type and concentration of electrolytes on clay suspensions flocculated with anionic polyacrylamides has been investigated. These polyacrylamides differ in terms of charge density and molecular weights. The presence of electrolytes was found to induce profound impact on the flocculation behaviour of clay-polyacrylamide dispersions, analysed by means of floc size distribution tests. Introduction of electrolytes exhibited a significant increase in the average floc size of the flocculated clay dispersions. Electric double layer compression and mediated flocculation by metal cations were predicted as the principle mechanisms involved in the improvement of flocculation behaviour. Divalent electrolytes were more efficient in enhancing the flocculation behaviour of clay-anionic polyacrylamide suspensions than monovalent ones. Apart from electrolytes, polymer characteristics also affected flocculation behaviour. The molecular weight of anionic polyacrylamides greatly influenced the floc size distribution. High molecular weight polymer chains increased bridging opportunities with clay particles producing larger flocs. Overall, this study successfully determines the effect of electrolytes on the flocculation behaviour of clay- polyelectrolyte suspensions.

**COLL 535**

**Unprecedented volume exclusion co-ion effect in self-assembly of macroions**

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Understanding the behavior of macroion in aqueous solution at a fundamental level has huge implications in various fields including biochemistry and material science. In dilute solution, certain macroions can self-assemble into hollow, spherical, single-layered, viral capsid-like, “blackberry”-type structures, which cannot be described by either Debye–Hückel theory for small ions or DLVO theory for colloids. The major driving force of this phenomenon has been found to be counterion-mediated attraction. Therefore, their solution behavior can be greatly affected by extra small counterions. Co-ions were believed to play less important role than counterions in controlling the self-assembly behavior of macroions. However, in this work, we have combined experiment and simulation to show that co-ions can actually have an unprecedented effect--bulky co-ions (Keggin-type polyoxometalates or boron clusters) can slow down or even fully inhibit the self-assembly of macroions (\{Mo72Fe30\} or \{SrPd12\}) in dilute solution and significantly decrease the sizes of blackberry structures. Co-ions do co-assemble with macroions and insert into the assembles. This new finding may provide a new sight on mechanism of polyoxometalate anti-virus ability, and various fields including colloids, biology and material science as well.

**COLL 536**

**Reverse binding affinities of metal cations in nanoconfined cavity**

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Metal cations are one of the most important ions in regulating solution behaviors of colloid particles. In aqueous media, the binding affinities of metal cations widely accepted in literature follow trends: Li⁺<Na⁺<K⁺<Rb⁺<Cs⁺ for monovalent cations and Mg²⁺<Ca²⁺<Sr²⁺<Ba²⁺ for divalent cations, which are regulated by their radius of hydrated ions. Herein we report that the widely-accepted trends of binding affinities for metal cations can be reversed in a nanoconfined cavity with high charge density and suitable size. We use a lacunary Keggin-type polyoxometalate K₇[α-PW₁₁O₃₉] as the model and study its ion-pair formation with metal cations by using isothermal titration calorimetry (ITC) and nuclear magnetic resonance (NMR) techniques. The results show that the hydration shells of metal cations will be destroyed significantly during their binding processes to the cavity, which leads to consequence that their binding affinities are more dependent on radius of bare ions rather than hydrated ions. As a result, the binding affinities of metal cations follow reversed trends: Li⁺<Na⁺<K⁺ for monovalent cations and Mg²⁺>Ca²⁺>Sr²⁺>Ba²⁺ for divalent cations in the cavity.
A model illustrating the reversed trend in cavity and widely-accepted trend outside the cavity.

COLL 537

Simple method for visual detection of lead (II) based on smart polymeric materials

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Lead is one of the toxic heavy metals that has serious harmful effects on human health. A simple osmotic device equipped with a commercial semi-permeable membrane and poly(N-isopropylacrylamide-co-benzo-18-crown-6-acrylamide) (PNB) nanogels is developed for visual detection of trace lead(II) ions (Pb$^{2+}$) in water. The device consists of an indicating pipe, a chamber filled with colloidal PNB nanogels solution and a semipermeable membrane fixed on the bottom of the chamber, just like a mercury thermometer. When the device is immersed into Pb$^{2+}$ solution, Pb$^{2+}$ will diffuse into the chamber spontaneously through semi-permeable membrane. 18-crown-6 groups in PNB nanogels and Pb$^{2+}$ will form stable positively charged complexes, and then the PNB nanogels swell due to the increase of hydrophilicity, which leads to the osmotic pressure increases. Driven by this osmotic pressure difference, more Pb$^{2+}$ solution outside device goes into chamber and the liquid level of the indicating pipe will rise. So the concentration of Pb$^{2+}$ can be detected by measure the change in the values of liquid level. The concentrations of Pb$^{2+}$ can be detected is as low as 10$^{-10}$ M. This method we proposed provides a novel avenue for visual detection of trace Pb$^{2+}$ for environmental protection.

COLL 538

Colloidal and chemical properties of graphene oxide and step wisely reduced graphene oxide

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Graphene Oxide (GO) contains different oxygen containing groups such as hydroxyl, carboxyl and epoxy. Oxygen containing groups can be removed chemically to reach reduced GO (rGO) which has different chemical and physical properties than GO. In following research chemical and colloidal behavior of rGO corresponding to different oxygen containing groups was studied. Starting with GO containing 49 percent oxygen, rGOs containing 31, 19 and 9 percent oxygen were reduced stepwisely. The aqueous behavior in terms of solubility gradually decreased from 7.4 μg/ml for GO to nearly zero for r-GO with 9% oxygen, while dispersibility under sonication decreased from 8 to 2.5 μg/ml for the same samples. Hydrophobicity index as measured as the octanol water partition coefficient decreased from −3.89 to 5.2% as oxygen content dropped from 49 to 9%. Colloidal behavior was also dramatically affected by reduction, and critical coagulation concentration (CCC) dropped from 28 to 15 in presence of 0.5 mmole/l NaCl and from 6 to 2 in presence of 0.5 mmole/l MgCl2 as the oxygen in the original GO was reduced to 9%.

COLL 539

Exploring the role of induced defects in carbon nanotubes through a novel camphor-mediated combustion approach in electromagnetic interference shielding application

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Tuning of the defect is critical for specific application of a material worth exploring and researching. In view of this, Additional defects inclusion in the form of rehybridization, twisted kinks, and fragmentation has been achieved in MWCNTs as well as SWCNTs fabricated through a unique camphor mediated combustion approach. Then they are further characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, high resolution transmission electron microscopy, and electron paramagnetic resonance. The significant defects induced in MWCNTs through combustion of camphor are unambiguously evidenced by their superior fluorescence quenching efficiency. Subsequently, we compared electromagnetic interference (EMI) shielding performance of SWCNTs vis-à-vis multiwalled carbon nanotube (MWCNT)-filled polystyrene (PS) nanocomposites. Interestingly, induced defects in SWCNT played a contrasting role with respect to MWCNT in their performance as EMI shielding materials. These findings have been correlated with the aspect ratio and percolation threshold of CNTs as well as dc conductivity of PS/CNT nanocomposites in the light of electromagnetic theory.

COLL 540

Ionic strength dependence of short DNA conformations at carbon nanotubes: Free energy landscape study
Single stranded DNAs are negatively charged biopolymers, which have been used to fabricate DNA-carbon nanotube (CNT) optical sensors. Polyelectrolyte nature of DNA leads to ionic strength dependence of its conformations. A recent study showed that optical response and phase transitions of DNA-CNT hybrids are dependent on the ionic strength. In particular, optical response of short ssDNA-wrapped CNTs becomes suppressed upon increase in salt concentration. Our computational results suggested that short DNAs may assume ring conformations around CNT, which in turn can lead to suppression of CNT optical response. Here, our recent free energy landscape calculations of short DNA structures at CNT suggest that DNA conformations at CNT change from helix to ring upon increase in salt-concentration. Accordingly, we believe that suppression of optical response of short DNA-CNT hybrids could be due to a helix-to-ring phase transition of DNA upon salt concentration increase. We hypothesize that this phase transition potentially changes exciton relaxation pathway at DNA-CNT hybrids from bright to dark one.

**COLL 541**

**Effect of the metal substrate on interlayer interactions in bilayer graphene**

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Bilayer graphene (BLG) has been shown to have advantageous electronic and physical properties relative to single-layer graphene (SLG) and is a model system for probing the tribology of graphene-based lubricants. However, few studies have investigated how metal substrates affect the interlayer interactions, as quantified by the exfoliation energy and sliding barrier of the upper graphene layer. In this work, we present a study of adsorbed BLG on several transition-metal surfaces using density-functional theory (DFT) incorporating the exchange-hole dipole moment (XDM) dispersion model. Our results show that physisorption of BLG on metal substrates does not significantly perturb the interlayer interactions. Conversely, chemisorption on metal substrates increases the exfoliation energies due to stronger dispersion contributions, which in turn affect the sliding energy barrier of BLG.

**COLL 542**

**Examining charge carrier mobility in graphene oxide-titanium oxide thin films**

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Thermoelectric devices have enabled the exploration of space for nearly 60 years. However, their utilization in Earth-based applications are limited due to the hazardous and expensive nature of current-state-of-the-art thermoelectric technologies along with their extremely low operational efficiency (approximately 6-7%). This work embodies an attempt at creating a new material possessing thermoelectric characteristics. This new material is based off of the graphene oxide-titanium oxide system, focusing on development of the interface for enhanced charge carrier mobility and density. The TiO$_x$-GO system has been investigated for a variety of applications over the last decade, including dye-sensitized solar cells, photovoltaics, lithium-ion batteries, and supercapacitors. While the structure, bulk electrical conductivity, and optical performance of this system has been explored quite extensively, the understanding of the nanointerfaces and their effects on the charge transport behavior in these systems are not well understood. This work begins to explore the interfacial interactions between graphene oxide (GO) and titanium oxide (TiO$_x$) in the form of thin films. TiO$_x$ is deposited onto a graphene oxide thin film via atomic layer deposition with tetraakis (dimethylamid) titanium (IV) (TDMAT) and water as the precursors. The amount of TiO$_x$ deposited and the temperature of deposition are statistically varied in order to explore the development of the interface between GO and TiO$_x$ and the effects that the TiO$_x$ structure have on the electrical transport properties. Structural and chemical analysis is coupled with in-plane and through-plane charge mobility and density measurements to elucidate the potential of such a material for thermoelectric applications.

**COLL 543**

**Anchoring Ti$^{4+}$/WO$_3$ onto functionalized graphene oxide: Enhanced adsorption capacity and photocatalytic activity**

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In this study, we fabricate Ti$^{4+}$ doped WO$_3$ hybrid composites and successfully anchor it onto reduced 3-methylanilintrimethoxysilane modified graphene oxide for Ti$^{4+}$/WO$_3$@GO-NH$_2$ photocatalysts. The structural, morphological, and photochemical properties of the obtained samples were thoroughly investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), N$_2$ adsorption/desorption, UV-vis diffuse reflectance (UV-vis DRS), thermogravimetric-differential thermal analysis (TGA-DTA), and Raman spectroscopy. And the photocatalysts could decompose rhodamine B dye under visible-light and exhibited higher activities than pristine materials. The excellent adsorption capacity and good reusability properties of the (Ti$^{4+}$/WO$_3$@GO-NH$_2$ suggest that it can be applied as novel adsorbents showing attractive commercial value.

**COLL 544**

Structure-dependent Fluorescence Resonance Energy Transfer (FRET) in aqueous, carbon, quantum-dots-embedded PC60-PC$_{61}$BM colloids
Going beyond the limit of a PC60 surfactant (fullerene molecule grafted with a polyethylene glycol (PEG) chain) structure, double-layer micelle formation, in waterborne colloids motivates exploration of new protocols to break out its morphology. In particularly, in the mixture particles combined with the PC60, it is more desired to afford efficient electronic interaction between the molecules in the absence of interruption of the PEG chains. In this respect, a new hybrid n-type nanosphere, carbon quantum dots (CD)-embedded PC60-PC61BM (PC60-CD-PC61BM) particles is established. Notably, the hybrid revealed a synthesis treatment-dependent particle structure, and the homogenizer-assisted PC60-CD-PC61BM allowed a watermelon-shaped spherical particle with stripe patterns, whereas a circular morphology randomly embedded CDs was observed in the microwave-assisted hybrid. More surprisingly, the watermelon-shaped colloid induced Fluorescence Resonance Energy Transfer (FRET) between the CD and C60 molecules, and the FRET-mediated emission signatures were gradually diminished when the stripe patterns were collapsed. In our work, thus, we can understand new carrier dynamics and a particle activity system in the developed concept of aqueous PC60-based colloids, which will be broadly utilized for eco-friendly technologies.

**COLL 545**

**Melt-rheology and morphology of multi-walled carbon nanotube-based polypropylene composites: Assessing the state of nanotube dispersion**

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Multi-walled carbon nanotubes (MWCNTs) incorporated polypropylene (PP) composites were prepared via a conical twin-screw micro-compounder, wherein MWCNTs were varied from 1-5 wt%. Morphological observation suggests 'agglomerate' dominated morphology in the respective composite, wherein 'remaining agglomerates' size is increased as a function of MWCNTs concentration. Oscillatory melt-rheological analysis indicates a rheological percolation threshold between 2-3 wt% of MWCNTs in the PP matrix, which manifested in the disappearance of the terminal behaviour in the lower frequency region of storage modulus versus frequency plot. In this context, it is to be noted that the influence of MWCNTs is more pronounced in the lower frequency region suggesting the dominant influence of various 'network-like' structures in the 'long-range' interaction between PP and MWCNTs. On the contrary, the respective composites show a lesser extent of 'short-range' interaction between PP and MWCNTs, in which all the composites merge to the value of pure PP in the higher frequency region. Further, MWCNTs were modified by a novel organic modifier (Li-salt of 6, amino hexanoic acid; Li-AHA) in combination with a polymeric compatibilizer (PP-g-maleic anhydride, PP-g-MA), which led to a higher fraction of 'individualized' MWCNT along with smaller
MWCNTs 'agglomerates' in the PP matrix. In the context, a systematic investigation has been carried out to understand the role of Li-AHA modified MWCNTs plus PP-g-MA on the morphology and melt-rheological behaviour of PP/MWCNTs composites. It is important to mention that Li-AHA modified MWCNTs along with PP-g-MA led to a significant change in the high frequency behaviour along with low frequency behaviour in storage modulus versus frequency plot suggesting the dominant influence of 'individualized' MWCNTs on the 'short-range' and 'long-range' interaction in PP/MWCNTs composites.

COLL 546

Carbon nanodots (CNDs): Fundamentals of the optoelectronic properties and antioxidation

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Carbon nanodots (CNDs) are a subset of the group of zero-dimensional carbon particles at size below 10 nm. CNDs contain a mixture of graphitic and diamond-like core surrounded with a variety of functional groups such as –OH, –CO, –COOH, –C=C, –NH2 depending on the precursor materials and synthetic methods (bottom up or top-down). Since their discovery, there have been many proposed applications for CNDs including bioimaging, drug delivery, solar cells, electrocatalysis and so on, due to their superior solubility, biocompatibility, tunable photoluminescence, and flexibility for structure and composite manipulation. However, there are controversial debates on the understanding of the origins of optoelectronic properties such as the fluorescence, photocatalysis and antioxidation. This report presents our recent results of CNDs on the optoelectronic properties and in photoelectric and bio-applications. Firstly, a new combined fluorescence-electrochemical approach is used to investigate optoelectronic properties of CNDs. Optical and electrochemical measurements along with the Hückel level calculations are applied to study the energy gap of CNDs which explains the origin of excitation wavelength dependent fluorescence of CNDs. The wavelength dependence of the photocurrent generation of immobilized CNDs is examined to assess the potential application in photoelectric devices. Secondly, a variety types of CNDs, by doping the nitrogen and/or sulfur or modifying the surface functional groups, are synthesized to study the structure-function relations and bio-applications focusing on antioxidation capacity in radical scavenging. A few antioxidation assays, including photo-spectroscopy of 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical, electrochemistry of DPPH, and lucigenin-CL assay for reactive oxygen species (ROS) produced through the xanthine/xanthine oxidase (XO) reaction, are used for the antioxidant capacity evaluation. The reaction pathways of the antioxidation of CNDs are proposed correlating to the structures of CNDs in the radical scavenging reactions. These findings provide new perspectives and knowledge on the structure-properties of CNDs and
should aid in their development for practical use in photoelectric devices and biomedicines.

**COLL 547**

**Confocal Raman microscopy investigation of small-molecule partitioning in hybrid supported bilayers**

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Hybrid supported lipid bilayers (HSLBs) deposited in reversed-phase chromatographic silica particles are a useful cell membrane model which can be utilized to predict the bioavailability of compounds and separate them based on their affinity for phospholipid membranes. In HSLBs, an upper leaflet of phospholipid molecules self-assembles on a lower leaflet of C₁₈-modified silica. Confocal Raman microscopy studies of these bilayers, within individual particles, have allowed for structural characterization of the membrane and quantification of a small molecule analyte partitioned into the bilayer. Unfortunately, although HSLBs are useful, phospholipids are expensive, and modifying an entire chromatographic column with phospholipids can be expensive. In this work, we propose an alternative hybrid membrane model where an upper-leaflet of surfactants is used in place of phospholipid. These hybrid supported surfactant bilayers (HSSBs) offer the benefit of lower cost and can provide a variety of head-group structures. To form a HSSB within a silica particle, we mimic a phospholipid by using two oppositely charged surfactants with similar headgroups and acyl chain lengths as a phospholipid molecule. Using Raman microscopy, the structure and melting transition of HSSBs was studied and compared with a HSLB, where similar structural characteristics were observed. Small-molecule toxicity, drug efficacy, and accumulation of molecules in biological systems can be predicted based on measurement of the phospholipid-water partition coefficient (Kₚ₦). Here, we demonstrate the use of HSSBs to measure phospholipid water partitioning of the small molecule naphthoic acid within an individual particle. The value of Kₚ₦ measured in HSSBs was compared to the value determined from the same measurement in HSLBs. The partitioning of naphthoic acid in both hybrid bilayers is similar. Finally, the pH dependence of naphthoic acid partitioning was measured. Here, partitioning depends on the pKₐ of the solute and the surface charge of the bilayer; by controlling pH, it was possible to determine the affinity of the neutral and anionic forms of the naphthoic acid. The resulting titration curve was used to calculate the pKₐ of naphthoic acid which was similar for both HSSB and HSLB. Interestingly, the measured pKₐ was lower than the pKₐ of aqueous naphthoic acid in aqueous due to the pH local to the interface as determined based on measurement of the interfacial zeta potential.

**COLL 548**
Surface chemistry and spectroscopic study of α-synuclein and its NAC part

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Parkinson’s disease is a very common neurodegenerative disease and characterized by a progressive loss of the dopaminergic neurons in substantia nigra. The degenerating dopaminergic neurons develop a hallmark deposition of Lewy bodies comprising abundant abnormal aggregates (i.e., fibrils) of α-synuclein (α-syn), which is a protein contains 140 amino acid residues. Despite the abundance (~ 1 % among the total proteins) in the brain, α-syn accumulates in the presynaptic terminals where exists high concentration of amphiphilic structure (e.g., lipsomes and cell membrane) and the reason of the accumulation is not clear. On the other hand, the primary structure of α-syn constitutes three domains: N-terminal residues 1–60; the nonamyloid component (NAC) which spans residues 61–95 and is responsible for the aggregation; and residues 96–140 which comprise the negatively charged C-terminus. Here, both α-syn and its NAC part (i.e., α-syn(61-95)) were synthesized and purified. α-Syn and α-syn(61-95) were shown to be able to form a stable Langmuir monolayer at the air-water interface, which has been widely used to mimic the amphiphilic structure in vivo. From circular dichroism results, both α-syn and α-syn(61-95) transform from unstructured conformation in aqueous solution to α-helix at the interface. In addition, surface FTIR techniques have shown a parallel orientation of the axis of the helix of both α-syn and α-syn(61-95) to the interface. Due to the high stability at the interface, no aggregation of α-syn(61-95) or α-syn has been detected.

COLL 549

Interactions of gold nanoparticles with phospholipid bilayer studied with coarse-grained molecular dynamics simulations

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Engineered nanoparticles (NPs) have extensive applications in the environment, bioengineering and energy industries. Gram-negative bacteria, such as Shewanella oneidensis have an asymmetric outer membrane, where the inner leaflet consists of phospholipids (mixture of phosphatidylethanolamine (PE) and phosphatidylglycerol (PG)) and the outer leaflet contains lipopolysaccharide (LPS). In this work, coarse-grained molecular dynamics (CG MD) simulations are preformed to study the interactions between an Au NPs and negatively charged S. oneidensis phospholipid (PE/P) bilayers in the aqueous environment. To achieve the fundamental understanding of the abiotic-biotic interface from the microscopic level, Au NPs are grafted with positive, negative and zwitterionic short-peptide chains. Several critical questions are addressed regarding the possibility of the formation of a lipid corona around a NP, lipid flip-flop and bilayer structural deformation, as well as water permeation and ion distribution during the course of NPs’ transmembrane process. In
addition, free energy computation are performed to quantify the NPs’ transmembrane barrier and driving forces.

**COLL 550**

**Novel route to designing radiofrequency and near-infrared responsive multifunctional nanostructures using lipid templates for cancer theranostics**

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We report a novel multifunctional delivery platform based on liposomes loaded with drug and super paramagnetic iron-oxide nanoparticles (SPIONPs), and covered with a gold shell that achieve multiple therapeutic objectives. The particles were synthesized using a lipid + polyelectrolyte (layersome) templating technique that protected cargo and facilitated shell formation. SPIONPs and the anti-cancer drug doxorubicin (DOX) were co-encapsulated inside liposomes composed by zwitterionic phosphatidylcholine (PC) and anionic phosphatidylglycerol (PG) using the reverse phase evaporation (REV) method. The liposomes were coated with positively charge polyelectrolyte (poly-L-lysine) to enrich the interface with gold anion, exposed to a reducing agent to form a gold nanoshell, and then capped with thio-terminated polyethylene glycol (SH-PEG2000). The core-shell nanostructures were characterized by different techniques and this multifunctional system achieves a variety of functions, such as radiofrequency-triggered release, chemo-hyperthermia, and NIR laser-triggered for photothermal therapy. Herein, we highlight some of the remaining design challenges in combination with preliminary studies assessing therapeutic objectives. We demonstrate an efficient loading of therapeutic content and then treatment of a human lung cancer cell line, A549, with passive and actively-triggered DOX release.

**COLL 551**

**Vitamin K analog, menaquinone-2, adopts a folded conformation in solution and at a model membrane interface**

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Menaquinones (naphthoquinones, Vitamin K, abbreviated as MK) are isoprenoids that play key roles in the respiratory electron transport system of some prokaryotes by shuttling electrons between membrane-bound protein complexes and act as electron
acceptors and donors. A truncated MK/Vitamin K analog, menaquinone-2 (MK-2), was synthesized and the studies presented herein characterize the conformation of the hydrophobic MK-2 molecule in various environments. Using 2D NMR spectroscopy, we established for the first time that MK-2 has a folded conformation defined by the isoprenyl side-chain folding back over the naphthoquinone in a U-shape, which depends on the specific environmental conditions found in different organic solvents. We used molecular mechanics to illustrate conformations determined from the 2D NMR experiments. Furthermore, MK-2 was found to associate with the interface of model membranes represented by Langmuir phospholipid monolayers and Aerosol-OT (AOT) reverse micelles. MK-2 adopts a slightly different U-shaped conformation within reverse micelles compared to within organic solution, which is in sharp contrast to the extended conformations illustrated in literature for MKs.

COLL 552

Understanding the role of interfacial and bulk interactions between novel cellulose ethers and bile salts to modulate lipid digestion

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Lipid digestion is a multistage process that relies up several interfacial and colloidal mechanisms to optimize lipid enzymatic hydrolysis (lipolysis) and transport processes. The adsorption of bile salts (BS) onto the oil-water interface of emulsions is a critical step for the progression of duodenal lipolysis. Hence, lipid digestion could be controlled ultimately by limiting the access of BS to the lipid surface, either by designing interfaces that resist displacement by BS, or by sequestering BS in the duodenum. The non-ionic and surface-active nature of cellulose ethers (CE) make them promising candidates to modulate lipid digestion. In order to investigate the role of CE molecular structure on the digestion of lipids at BS concentrations relevant to physiological conditions within the duodenum, the aim of this work is to study the interactions between diverse CE and BS in two different scenarios that emulsions find on their passage through the duodenum, namely the interface and the bulk.

Commercial hydroxypropyl-cellulose (HPC) and novel HPC-derivative (HPC-P), which contains a moderate balance of hydrophobic/hydrophilic substituent groups and negative charge at physiological pH, were studied. HPC-P was prepared through mild, versatile olefin cross-metathesis chemistry. We used surface-analysis techniques (QCM-D and SPR) to explore the formation of CE-BS layers onto hydrophobic surfaces by means of sequential adsorption, as representative of interfacial interactions, and simultaneous adsorption, to study the ability of CE to bind BS in solution. Sodium taurocholate (NaTC) and taurodeoxycholate (NaTDC) were chosen as representative BS with different hydrophobicity degree. Results showed that, despite the more
hydrophobic character of HPC-P enhanced its adsorption onto the surface, HPC-P adsorption was highly reversible with more than 50% of HPC-P being removed during the buffer exchange, which led to a lower surface concentration compared to HPC. However, novel HPC-P was more resistant to displacement by BS (NaTC and NaTDC) than commercial HPC at high BS concentrations. The more hydrophobic NaTDC showed a greater displacement of both CE from the surface than NaTC. CE-BS bulk interactions seemed to impact the ability of CE-BS complexes to disrupt BS adsorption at the hydrophobic surface. These findings provide valuable information on how CE could be tailored and exploited into both novel food and pharmaceutical matrices to modulate lipid digestion.

COLL 553

Interaction of surfactant with model lipid membranes: Influence of surfactant hydrophobic chain fluidity

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Skin becomes a target of drug delivery because the transdermal routes are non-invasive, can be self-administered, improves patient compliance and can provide release for long periods of time. The hydrophobic interaction between drug carrier and lipid layers has been accepted as one possible mechanism for changing the lipid packing in Stratum Corneum (SC), which leads to the enhancement of skin permeability. In general, hydrophobic interaction is extensively influenced by the hydrophobic chain length of the surfactant based drug carrier. However, the influence of surfactant hydrophobic chain fluidity is not fully understood yet, which is a key requirement for designing high-efficiency drug delivery system. In this work, neutron reflectivity (NR) is used to provide insights into the interactions between oleyl bis(2-hydroxyethyl)methyl ammonium bromide (OHAB), cetyl bis(2-hydroxyethyl)methyl ammonium bromide (C16HAB), stearyl bis(2-hydroxyethyl)methyl ammonium bromide (C18HAB) and isostearyl bis(2-hydroxyethyl)methyl ammonium bromide (IHAB), and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) monolayer. The results indicate that the phospholipids were depleted by the surfactants mainly through hydrophobic interactions. The interaction gradually increases in the order of C16HAB, C18HAB, OHAB and IHAB, which perfectly coordinates with the fluidity of these molecules. The ability of a surfactant to associate with skin lipids to form water-dispersible micelles was found to be a function of the hydrophobic chain fluidity. This work provides important advances in understanding the mechanism of lipid-surfactant interaction from the fluidity of molecules, which can ultimately contribute to the development of surfactant based drug carrier.
Figure 1. NR profiles for deuterated DPPC monolayer (spread at 28.0 mN/m) at the air-NRW interface, and with the presence of h-C_{16}HAB, h-C_{18}HAB, h-OHAB and h-IHAB. The solid lines are fits to the data with one-layer model. The insert shows the corresponding scattering length density profiles for calculated reflectivity profiles.

**COLL 554**

**Ligand density and conformation on gold nanoparticles inferred by NMR**

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Molecular ligands stabilize colloidal nanoparticles in water and also tune their surface chemistry. NMR is a standard chemical method that, when applied to molecularly-capped colloidal nanoparticles larger than about 5 nm, usually results in either in no signal (because the sample is too dilute) or aggregated particles at the bottom of the NMR tube. We report NMR results of ligands on gold nanoparticles, 1-25 nm diameters, concentrated 100x as usual without aggregation, and measure headgroup mobility and ligand density as a function of particle diameter. Molecular dynamics simulations support the notion that ligands are more densely packed, but less ordered, on smaller nanoparticle surfaces.

**COLL 555**

**Improving the stability of CsPbX\textsubscript{3} (X=Cl, Br, I) perovskite quantum dots via ligand design**
Colloidal perovskite quantum dots (PQDs), in particular those made of full-inorganic CsPbX$_3$ (X = Cl, Br, I), have attracted tremendous attention over the past few years, due to their excellent optoelectronic properties and the promise they offer in applications that include light-emitting and photovoltaic devices. However, such potential is hampered by their very limited steric stability and rapid loss of fluorescence during processing. These problems are caused by a combination of the ionic nature of the cores and fast desorption of the surface capping ligands. To address those problems, we have developed a ligand exchange strategy based on substituting the native cap with a multifunctional polymer where surface coordination is driven by electrostatic interactions (using zwitterion moieties).

The ligands were synthesized by installing a stoichiometric mixture of zwitterion and solubilizing motifs on a poly (isobutylene-alt-maleic anhydride), PIMA, via nucleophilic addition reaction. We find that this coating exhibits strong binding affinity to the ionic surfaces of the PQDs, and imparts enhanced colloidal stability of the nanocrystals over a broad range of solvents, including those with high polarity. As such, dispersions of PQDs in several alcohols, with preserved cubic crystal structure and superior photophysical properties (namely, narrow-band emission and high photoluminescence quantum yield) have been prepared and tested.

**COLL 556**

**Small angle x-ray scattering for sizing of semi-conducting colloidal nanoparticles**

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Gaining quantitative structural insight at the nanoscale is an important issue in nanotechnology where size effects play a prominent role. Alongside electron microscopy, scattering techniques can be used to provide such information in solution and at the ensemble level. During this talk, I will first recall the basic theoretical and experimental aspects of (small-angle) X-ray scattering. I will then illustrate these concepts with recent examples in nanoparticle research where the use of X-ray scattering proved efficient. Notably, we recently measured precisely the size of series of PbS, PbSe, CdS and CdSe colloidal nanocrystals [1]. By measuring alongside their absorption spectra, we could set-up calibration curves relating their energy band gap to their diameter. We will discuss these results and compare them with previous calibration curves determined by TEM. Finally, we will show that it is also possible to measure accurately the concentration of nanoparticles in solution.
Colloidal atomic layer deposition

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In contrast to molecular systems, which are defined with atomic precision, nanomaterials generally show some heterogeneity in size, shape, and composition. The sample inhomogeneity translates into a distribution of energy levels, band gaps, work functions, and other characteristics. The lack of atomistic control during nanomaterial synthesis also limits our ability to perform “total-synthesis” of sophisticated nano-heterostructures with precisely arranged multiple components and fine-tuned properties. We discuss a general synthetic strategy which largely circumvents these limitations of traditional colloidal synthesis. Colloidal Atomic Layer Deposition (c-ALD) allows a significant reduction of inhomogeneity for nanomaterials without compromising their structural perfection. We report a novel realization of c-ALD step sequence which significantly improves synthetic control and quality of synthesized nanomaterials. In traditional gas-phase ALD, the substrate and gaseous reactants act as the stationary and mobile phases, respectively. Such distinction facilitates removal of unreacted precursors by pulsing inert gas after each half-reaction. For c-ALD, we inverted the stationary and mobile phases – reactants form the stationary phase while the substrate is moved in and out of the reactor as the mobile phase. This approach brings c-ALD closer to traditional ALD and is expected to make it a similarly powerful and versatile technique. Our improved c-ALD enables synthesis of epitaxial nano-heterostructures of unprecedented complexity, ultimately enabling bandgap and strain engineering in colloidal nanomaterials synthesized with close-to-atomistic accuracy. Improved synthetic control elucidates the effects of quantum confinement and strain on the properties of semiconductor nanostructures.

Surface chemistry of colloidal Cu$_{2-x}$S and CuInS$_2$-based nanocrystals

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Colloidal nanocrystals (NCs) of compound Cu-chalcogenides are an interesting class of materials, and have been attracting increasing attention as alternatives to Cd- and Pb-chalcogenide NCs, since they have low toxicity, potentially lower costs, and a very wide range of compositions and crystal structures. These nanomaterials differ in many ways from the prototypical II-VI and IV-VI semiconductor NCs, and are still poorly understood. For example, in contrast to II-VI and IV-VI semiconductors, they tolerate large stoichiometry deviations and accommodate significant excess carrier densities, being easily p- or n-doped. Moreover, their optical spectra are characterized by broad
bandwidths (~200-400 meV) and large global Stokes shifts (~300-500 meV), and the radiative exciton lifetimes are very long (hundreds of ns). Their surface chemistry is also dramatically different from that of II-VI and IV-VI semiconductor NCs, being characterized by a very dynamic inorganic surface and strong interactions with certain types of ligands (e.g., alkylthiols). As a result, their inorganic-organic interface is much more dynamic and complex than that of the II-VI and IV-VI analogues.

In this talk, I will discuss the surface chemistry and the inorganic-organic interface of these colloidal nanomaterials, using Cu$_{2-x}$S and CuInS$_2$ NCs as representative examples, and focusing on three different processes: cation exchange, heteroepitaxial shell overgrowth and ligand exchange. The dynamic character of the inorganic surface of these nanomaterials, associated with high solid state diffusion rates, has been exploited in post-synthetic topotactic cation exchange reactions, leading to a variety of nanomaterials that cannot be attained by conventional methods. However, this also makes the synthesis of CuInS$_2$-based core/shell NCs challenging, because cation exchange and alloying reactions compete with heteroepitaxial shell overgrowth. We recently demonstrated that the latter process can be made dominant by using a combination of reactive precursors, high reaction temperatures, and acetate ligands at the surface of the CuInS$_2$ NC seeds. We have also taken advantage of the interaction of specific ligands with the surface of CuInS$_2$ NCs to induce anisotropic ZnS shell growth or formation of In-poor CuInS$_2$ nanosheets by self-organization. Finally, ligand exchange has also been explored in our work, both as a way to render Cu$_{2-x}$S and CuInS$_2$ NCs water-dispersible, and to construct FRET nanoprobes.

**COLL 559**

Interrogating, J, spectral overlap in terbium(III) doped nano-spinels as green emitters for solid-state lighting

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Down-shifting phosphors are routinely used in solid-state lighting to convert higher energy UV or blue light to visible light. However, color quality of commercial LEDs are modest and new RGB phosphors are needed to tune the color of light. Commercial LEDs are composed of bulk semiconductors that typically contain materials on the DOE high risk index. For improving performance of down-shifting phosphors, size of the phosphor must be reduced to sub 10nm to reduce scattering of the pump led, the host lattice must be composed of earth-abundant materials, and must absorb pump LED irradiation and convert to pure red, green, and blue emission for optimal color quality. Here we present the microwave synthesis of nanophosphors doped with Terbium(III) to accomplish green emission. Lanthanide emission is accomplished by energy transfer from surface ligands to lanthanide metal centers by using the molecular antenna effect. Optical measurements of the nano-spinel will be discussed including absorption, emission, lifetime, and quantum yields. Ligand exchanges were completed in efforts to
improve quantum efficiencies and the nanospinels were characterized by pXRD, TEM, EPR, and FT-IR.

COLL 560

Understanding uniform, fast and scalable buoyancy-driven macro-sized drop generations

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Uniform drop has been crucial academic and industrial building blocks for various applications such as food, cosmetics, home- and personal care, and more particularly for pharmaceutical applications in drug delivery or radiology. Most of the research firms in the fields of chemistry also demand high monodispersed drops with tunable size, because the uniformity of drop can have significant consequences for the responsive behavior and properties of the end product.

Recent studies for the drop focus on microfluidic technique, but it faces challenges during the attempts to scale up the technology to mass production. The production rates of the technology are 1-10kHz, but the microfluidic devises are hindered in commercialization for reasons such as the presence of continuous phase flows, small cross-sectional area, and very small flow rates. As a result, microfluidic approaches fail to satisfy the productivity requirement of standard yield, ~ 1000 t/y.

The formation processes of millimeter-sized drops were recently re-highlighted in a buoyancy-driven system that is feasible for both fundamental studies and industrial applications because there are fewer governing forces and variables affecting the drop formation than the microfluidic processes.

In this study, we propose a strategy to produce milli-scale drop. Uniform drops are selectively generated with controlling flow rate, channel diameter, affinity of membrane to the drop and their range of the production rates was ~ 0.1-2.1 Hz. The pinch-off time and force dynamics for drop generation are different according to the affinity between drop and membrane surface. It appears as different initial contact angles (whether larger or smaller than 90°) and results in the different diameter and frequency of the drops in same channel diameter. These phenomena are investigated by our novel model. On hydrophobic membranes, the diameter range of the uniform drops is wider (from ca. 5.7 to 10.4 mm) than that on hydrophilic one (from ca. 3.8 to 7.0 mm). However, on the hydrophilic membranes, the smaller drops are fastly generated in terms of the production rate than those of the hydrophobic membrane.
Mechanistic modeling of wetting behaviors of complex rock/oil/water systems for estimating rupture disjoining pressure: A comparison of experimentally-estimated values with published, theoretically derived values

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The present study reports on a comparison of measured ambient condition (atmospheric pressure and laboratory temperature) values of adhesion energy per unit volume, which can be mechanistically correlatable to rupture disjoining pressure, with the maximum values of disjoining pressure derived from theoretical disjoining pressure curves for certain rock/oil/water systems that have been reported in the published literature (Jalili and Tabrizy, 2014). The rock/oil/water systems compared here showed varied degrees of wetting characteristics, as inferred from the sessile oil drop volume alteration experiments that were performed in order to collect the necessary dynamic water-receding and water-advancing contact angle data. The results presented in Table 1 indicate that experimentally-measured values are significantly higher than the theoretically-derived values. This observed difference may be attributed either to the uncertainty associated with the theoretically-derived aqueous phase thickness value that was used in the calculations, or possibly to the inability of theoretical models to calculate rupture disjoining pressure beyond certain values. For weakly water-wet to intermediately-wet systems, both the theoretical (disjoining pressure curve) and the experimental (adhesion energy/volume) approaches reasonably agreed. However, in the case of oil-wet systems, each approach results in significantly different values. Thus, the experimental results obtained in the present study can be used to further refine the existing theoretical models or to develop new disjoining pressure models for the complex rock/oil/water systems that exhibit oil-wet wetting behaviors.
Table 1: Comparison of ambient condition experimentally-estimated values of adhesion energy per unit volume (equivalent to rupture disjoining pressure) for complex rock/oil/water systems with published theoretically-derived values.

<table>
<thead>
<tr>
<th>Rocks/Oil/Water System</th>
<th>Theoretically-derived (Jalili and Tabrizy, 2014) Aqueous Phase Thickness, ( h ) (nm)</th>
<th>Theoretically-derived (Jalili and Tabrizy, 2014) Maximum Disjoining Pressure, ( \Pi(h) ) (atm)</th>
<th>Measured (This Study) Adhesion Energy/Volume ( \Delta E_{\text{adhesion}} ) (atm)</th>
<th>Ratio of Measured Adhesion Energy per Unit Volume to Theoretically-derived Maximum Disjoining Pressure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz modified with 0.35 wt % Asphaltene/( n )-Decane/Distilled Water</td>
<td>0.6</td>
<td>200 (attractive)</td>
<td>1394 (Trial 1) to 12.58 (Trial 2) (attractive)</td>
<td>7.0 (Trial 1) to 6.3 (Trial 2)</td>
<td>Strongly Oil-wet System</td>
</tr>
<tr>
<td>Quartz modified with 0.35 wt % Asphaltene/( n )-Decane/0.1M NaCl</td>
<td>0.9</td>
<td>200 (attractive)</td>
<td>645 (Trial 1) to 775 (Trial 2) (attractive)</td>
<td>3.2 (Trial 1) to 3.9 (Trial 2)</td>
<td>Strongly Oil-wet System</td>
</tr>
<tr>
<td>Calcite modified with 0.35 wt % Asphaltene/( n )-Decane/Distilled Water</td>
<td>0.9</td>
<td>200 (attractive)</td>
<td>556 (Trial 1) to 1060 (Trial 2) (attractive)</td>
<td>2.8 (Trial 1) to 5.3 (Trial 2)</td>
<td>Weakly to Moderately Oil-wet System</td>
</tr>
<tr>
<td>Calcite modified with 0.35 wt % Asphaltene/( n )-Decane/0.1M NaCl</td>
<td>1.8</td>
<td>200 (attractive)</td>
<td>154 (Trial 1) to 275 (Trial 2) (attractive)</td>
<td>0.8 (Trial 1) to 1.4 (Trial 2)</td>
<td>Weakly Water-wet to Intermediately-Wet System</td>
</tr>
</tbody>
</table>

Coll 562

Spontaneous displacement of high viscosity micron-size oil droplets from a curved solid in aqueous solutions

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Spontaneous displacement of high viscosity (~10³ Pa•s) micron size oil droplets from a curved solid in aqueous solutions was investigated using an optical method. From the
image analysis, the dynamic droplet shape of the high viscosity oil was found to departure significantly from a spherical cap shape due to the considerable viscous force in the oil phase. As such, the "quasi-static spherical cap approximation" that is often used to calculate dynamic contact angles cannot be applied. To analyze the displacement dynamics of high viscosity droplets using molecular kinetic and hydrodynamic models, here alternative methods are proposed to determine dynamic contact angles. The molecular kinetic model was found to describe the dynamic displacement well for the droplets of small departure from the spherical cap shape, while the hydrodynamic model is more applicable to larger deviation of the droplets. This research has improved our understanding on microscale liquid-liquid displacement under considerable viscous force and expanded comprehensive knowledge of spontaneous wetting phenomenon to systems with high viscosity fluids, such as polymer melts or heavy crude oil.

**COLL 563**

**Structural and dynamic properties of Ionic liquid-solid interfaces**

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Ionic liquids (ILs) are organic molten salts with low melting points, which typically feature incommensurate amphiphilic ions, which hinders crystallization in the absence of a solvent over a wide range of temperatures. Besides the growing interests in applying ILs in micro electromechanical systems and novel composite materials, ILs also provide unique opportunities to examine the fundamental principles that dictate the
properties of solid-liquid interfaces. Specifically, they enable to study the interplay between charge-driven interactions (Coulombic force) and density-driven interactions (entropy and excluded volume) in the absence of molecular solvents. In this study, we contribute to the current discussion about the electrostatic interactions in ILs that is under heated debate. Through normal and lateral force measurements by surface forces apparatus (SFA) and atomic force microscopy (AFM), we approach the question from the perspective of equilibrium structures and of dynamic behavior. In particular, we show that the viscosity of confined ILs has a universal dependence on electrostatic interactions. Further, water is introduced at varied concentrations as an impurity that significantly changes the interfacial structures and we describe how the water molecules alter both the equilibrium nanostructures and the dynamic response of the ILs.

**COLL 564**

**Spreading of wetting liquids on surfaces with irregular roughness**

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A wetting liquid can spread on a rough surface due to capillary forces drawing the liquid into the surface roughness features. When the surface roughness is due to a regular pattern, such as a micropillar array, the liquid front is sharp and its dynamics can be modeled with a first-order ordinary differential equation similar to Washburn’s equation. However, when the surface roughness is highly irregular, the liquid front is diffuse and a partial differential equation must be used to determine the variation of liquid saturation on the surface. In this work, an unsaturated flow model similar to what is employed for groundwater flows, is used to describe liquid spreading on a rough surface. Both key model parameters, the capillary pressure and permeability, are nonlinear functions of local liquid saturation, and these are determined experimentally for a series of n-alkanes on a polyurethane-based composite coating. Time-resolved Raman spectroscopy is used to determine the variation in intensity of Nile red dye dissolved in the n-alkanes over the surface of the material when one end is immersed in the liquid solution and the liquid moves one-dimensionally along the surface. The resulting liquid saturation vs. position curves are used in a multiobjective nonlinear fit of the unsaturated flow model parameters. The fit model can be used to predict the dynamics of liquid motion over the rough surface in many different scenarios, including droplet spreading.

**COLL 565**

**Droplets sliding down a vertical surface under increasing horizontal forces**

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We have investigated the retention force on a liquid drop that is placed on a rotating, vertical surface. We considered two scenarios: In one, a horizontal, centrifugal force pushes the drop towards the surface (“pushed drop” case), and in the other, a horizontal, centrifugal force pulls the drop away from the surface (“pulled drop” case). Both drops slide down as the centrifugal force increases, although one expects that the pushed drop should remain stuck to the surface. Even more surprising, when the centrifugal force is low, the pushed drop moves faster than the pulled drop, but when the centrifugal force is high, the pushed drop moves much slower than the pulled drop. We explain these results in terms of interfacial modulus between the drop and the surface.

**COLL 566**

**Interactions at submerged liquid-repellent surfaces: Gas meniscus formation and development**


The long-range attractive interactions between hydrophobic surfaces in water have been attributed to the formation of a bridging gas meniscus via cavitation (i.e. vaporization of the surrounding liquid) and/or by the existence of nanobubbles. The range of these interactions is typically in the order of tens to hundreds of nanometers. On superhydrophobic surfaces the range of such attractive interactions can exceed 10 μm. These much longer ranged forces have been explained by the pre-existing air-layer at the superhydrophobic surface allowing the formation of a large and growing meniscus. However, the development of the meniscus volume and the shape of the interface between the gas phase and the liquid have so far been unclear. In this work, we aim to contribute to the understanding of the underlying mechanisms of interactions taking place at submerged liquid-repellent surfaces. We use laser scanning confocal microscopy (LSCM) to image gas meniscus formation between a liquid-repellent coating and a microsphere in liquid, while simultaneously measuring the interaction forces using colloidal probe atomic force microscopy (AFM). The confocal images allow determination of the meniscus volume and shape, and show an increase in the meniscus volume with separation as air is transported from the pre-existing air-layer underneath the interface between the coating and the liquid. How the shape of the meniscus develops during separation can depend on the liquid surface tension, the air-
layer thickness, and on local micro/nanoscale pinning sites. Single pinning events are too small to be identified in macroscopic wetting experiments such as contact angle hysteresis and roll-off angle measurements, but can be resolved in our microscale experiments.

COLL 567

Dynamic surfactant behaviour and interface coverage during single droplet formation in microfluidics

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Dynamic surfactant behaviour is of paramount importance in industrial and research application. Microfluidic droplet formation is a dynamic process that involves the use of surfactants for the stabilisation of the produced droplets. It has been shown that during droplet formation surfactant molecules rearrange on the interface creating concentration gradients that lead to surface tension gradients that affect droplet formation. We use a microfluidic setting to study the surfactant rearrangement during droplet formation. We have shown that surfactants with smaller molecular weights, therefore larger diffusion coefficients, are more capable in coping with the short time scales of droplet formation present in microfluidics. This has been done by examining the velocities along the interface moments before detachment. Interfaces where surfactant is present display velocities smaller than surfactant free interfaces. Furthermore, the number of satellite droplets produced appears to be increasing with increasing surfactant concentration, suggesting additional effects, even at concentrations above the critical micellar concentration.

COLL 568

Porous liquid infused surfaces in microfluidics: Pressure and heat transfer measurements

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Porous liquid infused surfaces, commonly referred to as SLIPS (slippery liquid-infused surfaces), can be any nano/microstructured porous solid material with a lubricated film used to create surfaces that exhibit liquid repellency, self-healing, optical transparency, pressure stability, and self-cleaning. If designed properly these surfaces can repel many fouling challenges including bacteria, ice, water, oil, dust, barnacles, or other contaminants, and have been proposed as coatings on industrial and medical surfaces. These surfaces are robust even under high temperature and pressure conditions which also positions them as a viable treatment for the walls of microelectronic cooling
channels or on fuel lines to reduce coking in high-temperature fuel delivery. To establish this use case, we present the development of a microfluidic device incorporating a porous liquid infused surface, and we measure the pressure drop and heat transfer across this surface while tailoring the chemistry, porosity and infusing liquid on the surface.

**COLL 569**

**Microscale droplets of thermotropic liquid crystals that respond to rhamnolipids and amphiphiles involved in the regulation of bacterial quorum sensing**

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We report the design and characterization of microscale droplets of a thermotropic liquid crystal (LC) that respond to amphiphiles produced specifically by large groups or ‘communities’ of bacteria. Past reports demonstrate that aqueous dispersions of LC droplets undergo changes in internal configurations upon the adsorption of amphiphiles in ways that can be observed using polarized light. This behavior forms the basis of strategies for the real-time detection of environmental amphiphiles, including those produced by bacteria. Here, we demonstrate that droplets of LCs undergo ‘bipolar-to-radial’ configurations on exposure to amphiphiles that regulate bacterial quorum sensing (QS), a process by which bacteria communicate and carry out group activities, such as biofilm formation and virulence factor production. We demonstrate that LC droplets undergo bipolar-to-radial transitions on exposure to a series of acyl homoserine lactones (AHLs) that regulate QS in Gram-negative bacteria. By increasing AHL tail lengths from 4 to 12 carbons, we demonstrate that the concentration of AHLs required to promote these transitions decreases, allowing the transition to occur at 10 µM for the 12-carbon N-(3-oxo-dodecanoyl)-L-homoserine lactone, a natural QS signal in *P. aeruginosa*. Our results also reveal that these droplets respond to biologically relevant concentrations of the biosurfactant rhamnolipid, an amphiphile produced only by communities of *P. aeruginosa* under control of QS. Additional studies demonstrate that these droplets do not undergo bipolar-to-radial transitions in bacterial cultures growing at low population densities, but do undergo configurational changes as the bacteria grow and reach ‘quorate’ populations. These and other systematic studies using genetically engineered knock-out strains support the conclusion that these LC droplets respond selectively to the production of rhamnolipid and amphiphiles involved in the regulation of QS, and not other products produced by bacteria at lower sub-quorate densities. With further development, readily dispersed and environmentally stable droplet-based LC sensors could prove useful for the real-time monitoring of bacterial growth and virulence. More broadly, our results provide guidance for the design of new
soft materials platforms that can sense, interact with, and respond selectively to large communities of bacteria engaged in collective group behaviors, including virulence factor production and biofilm growth.

**COLL 570**

**Design of chiral gold nanoparticles for biosensing**

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Gold nanoparticles have been investigated for biosensing due to their strong surface plasmonic behavior which can be tuned by the refractive index of surrounding media. The chirality of gold nanoparticles can be induced by the interaction between chiral molecules and gold atoms during the growth step. Their chirality can be controlled by amino acids with factors of handedness, species and concentration. The seed-mediated method allows us to produce more complex chiral nanostructures in a well-controlled fashion, and the synthesized chiral nanostructures show higher-order chiral characteristics in visible light. The nanostructure was analyzed by 3D reconstructed images from scanning transmission electron microscopy tomography, which can help to understand the optical features. Since spectra of circular dichroism exhibit narrower bandwidth than that of absorbance, the chiral nanoparticles allow us to sense the biomolecules effectively. Potentially, it enables us to use the chiral nanostructures for multiplex biosensing.

**COLL 571**

**Shaping magnetic fields for effective drug transport across liposome membranes**

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There is great interest in the scientific community and pharmaceutical industry in developing mechanisms to control biological processes at the cellular level. A particularly intriguing concept is to regulate material transport across biologically important membranes by external magnetic stimuli. In this work, we demonstrate the ability to prepare liposomes loaded with model drug and magnetic particles. The magneto liposomes when triggered with inhomogeneous pulsed magnetic fields release drug molecules. We have discovered that the mechanism of drug release is the result of the ultrasound generation from small magnetic nanoparticles. The ultrasound is generated from the movement of particles in inhomogeneous magnetic fields as opposed to the much weaker magnetostriction effect due to homogeneous magnetic fields. While magnetic heating from low frequency is also used for drug release from liposomes, this work has achieved comparable efficiency on the sub millisecond time scale using intense pulsed magnetic fields (few Teslas) as opposed to extended use of low frequency magnetic fields. While inhomogeneous magnetic pulses provide an
effective tool, we also have developed a homogeneous rotating magnetic field generator that will be used in the next phase to generate mechanical motion from directional change of anisotropic magnetic structures. Preliminary data on the characterization the rotating magnetic field generator is also shown.

COLL 572

Aqueous 0D, 1D, and 2D semiconductor nanocrystals: Single nanoparticle analysis and bioimaging applications

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Semiconductor nanocrystals have been extensively applied in bioimaging due to their unique and tunable electronic and optical properties. While the vast majority of these applications have used zero-dimensional quantum dots (QDs), newer one-dimensional nanorods (NRs) and two-dimensional nanoplatelets (NPLs) can provide a wide range of useful optical properties, including narrow-band and polarized emission. However, transferring these anisotropic from organic solvents after synthesis to aqueous solution poses major challenges due to their high surface area to volume ratios. In this study, we develop a general strategy to prepare water-dispersible QDs, NRs, and NPLs using multidentate polymers. The resulting aqueous nanocrystals are homogeneous in hydrodynamic dimensions based on gel permeation chromatography (GPC) and can be efficiently conjugated to a wide range of biomolecules using processes already optimized for conventional QDs. We analyzed the single-molecule properties of each of these nanomaterials classes to determine their benefits and weaknesses for a variety of bioimaging applications, focusing on flow cytometry and immunolabeling. Interestingly, biomolecular conjugates of NRs and NPLs showed much faster binding kinetics compared QDs of similar volume and compared with organic dyes. This phase transfer strategy extends the applications of anisotropic semiconductor nanocrystals in biology, and can help to enable a new understanding of cell-nanomaterial interactions.

COLL 573

Antimicrobial-peptide-conjugated MoS₂-based nanoplatform for multimodal synergistic inactivation of superbugs

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Development of new antibacterial therapeutics material is becoming increasingly urgent due to the rapid emergence of antibiotic-resistant superbugs, which are responsible for more than half million death each year in this world. Here we will discuss our current reports on the development of novel nano-biomaterial based on melittin antimicrobial peptide (AMP) attached transition metal dichalcogenide MoS$_2$ based nanoplatform for targeted identification and synergistic inactivation 100% multidrug-resistant superbugs by combined photo thermal therapy (PTT), photo dynamic therapy (PDT) and AMP process. Our report shows that due to the presence of AMP, multifunctional AMP exhibits significantly improved antibacterial activity for superbugs via multimodal synergistic killing mechanism. Experimental results show that i 100% of carbapenem-resistant (CRE) Escherichia coli, β-lactamase (ESBL) – producing Klebsiella pneumoniae (KPN) and Methicillin-resistant Staphylococcus aureus (MRSA) can be killed using antimicrobial peptide attached MoS$_2$ QDs, via synergistic killing mechanism. Possible mechanisms for synergistic killing of multidrug-resistant superbugs will be discussed.

COLL 574

Surface-supportive Fe-Mil88B thin films for drug delivery

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Coronary artery disease contribute to 25% of all deaths nationally. To treat symptoms of this disease, polymer-based drug eluting stent coatings have been developed and have exhibited great advantages over bare metal stents alone. However, clinical studies have shown the polymer coating has been linked to numerous cases of hypersensitivity reactions and inflammatory responses. Our goal is to replace the polymer with an iron-based metal organic framework (Fe-MOF) due to its non-toxicity, high porosity, and biodegradable characteristics. Specifically, we used MIL-88B which is composed of iron ions connected by organic ligands forming a 3D cage like structure. One of the greatest advantages to using a Fe-MOF is the ability to chemically bond to metal and functionalized metal surfaces. Our approach involves a three-step method starting with the synthesis of MIL-88B. Gold and medical grade stainless-steel (SS) were used as metal substrates to obtain uniform surface-supportive thin films by a direct crystallization method. Lastly, ibuprofen was used as a model drug to test for their drug encapsulation and release kinetics capabilities. We applied surface analytical techniques, including X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared (FT-IR) Spectroscopy to analyze the elemental composition as well as for chemical characterization of the thin films. After confirming the chemical compositions of the thin films, we loaded a solution of ibuprofen/hexane onto the Fe-MOF thin film through a simple submersion technique. The drug loading capacity was analyzed by measuring the ibuprofen/hexane solution before and after incubation by UV-Vis spectroscopy, and drug release kinetics by High Performance Liquid Chromatography. In summary, the Fe-MOF thin film was confirmed to grown onto gold and SS demonstrating successful encapsulation of ibuprofen into the MOF structure. Our preliminary findings are...
significant and show promise in increasing the understanding of MOF thin film formation on a medical device as a drug delivery system.

COLL 575

Physicochemical characterisation of PAMAM dendrimer as multifunctional nanocarriers

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Dendrimers are a special class of polyelectrolytes, which are characterized by their densely branched and well-defined spherical geometry. Amino-terminal dendrimers resemble spheres, whose uniform surface charge densities can be continuously modulated by pH or ionic strength. Dendrimers have a wide range of applications, including biomedical applications such as drug delivery, gene delivery, cancer therapy and diagnostic agents. Their unique properties originate in their macromolecular structure. It is known that dendrimers can undergo irreversible swelling, and this process is directly connected to the degree of protonation of dendrimer molecules. The hydration of dendrimer films seems to be a crucial aspect of their implementation. In all biological systems, the conformational stability is intrinsically connected with natural hydration. Therefore, the estimation of the degree of hydration in dendrimer films on a model surface is essential for the study of their potential applications.

The present study focuses on the structure of dendrimer monolayers on gold surfaces. We used multi parametric surface plasmon resonance (MP-SPR) and a quartz crystal microbalance with dissipation energy monitoring (QCM-D) to investigate the conformational behaviour of the 6th generation of PAMAM molecules. The combination of MP-SPR and QCM-D measurements allows the investigation of factors that govern the immobilization of PAMAM dendrimers on a gold coated sensor surface. Changes in pH have a strong effect on the binding affinity of the polymer to the surface and additionally, indicate very different conformation behaviours. The trends in the binding affinity and the surface saturation amount correspond well with the degree of change of protonation of the adsorbed molecules. This data very clearly indicates how the structure of the dendrimer can influence the properties of the polymer film formed on the gold surface. PAMAM films on gold surfaces are composed of 80% water. This is a particularly large value compared to the amount of water associated with the dendrimer molecules during the swelling process, which was estimated at 25-30%. This is one of the additional advantages of dendrimeric systems.

These investigations lead to a more profound understanding of the self-assembling behaviour of branched polyelectrolytes, which are interesting candidates for reversibly tunable swelling materials for drug delivery or smart molecules for surface functionalization.

COLL 576
Dynamic liquid colloids: A new sensing material for the rapid detection of foodborne pathogens

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Multiphase complex emulsions formed from two or more immiscible solvents offer a unique platform as new materials for chemical sensor applications. The temperature controlled miscibility of fluorocarbons (F) and hydrocarbons (H) enables a temperature induced phase-separation, leading to structured emulsion droplets of H and F in water (W), which can be alternated between encapsulated (F in H, and H in F), and Janus configurations by varying the interfacial tensions using surfactants. These complex emulsion droplets can selectively invert morphology in response to external stimuli such as the presence of specific analytes, small pH changes, visible light or high energy irradiation, and the presence of an electric or magnetic field. This, in combination with the unique optical properties of these emulsion droplets enables the application of complex emulsions as a new transduction material for chemo- and bio-sensing applications. Here, we will show examples of how the addition of stimuli-responsive surfactants to the complex emulsions provides a method to induce morphological changes or variations in the droplet alignment in response to the presence of specific chemical or biological analytes. In order to create an optical read-out, emissive dyes were added to one of the two immiscible phases of the complex emulsions. As a result, the unique chemical-morphological-optical coupling inside these complex emulsions led to the development of a series of new optical transduction methods. Specifically, the adjustment of the refractive indices of the two solvents resulted in a new unprecedented control of light propagation inside the emulsion droplets. Gaining control over the potential of these micro-colloids to manipulate light in form of waveguides paved the way towards the development of easily deployable liquid sensing platform that allow for the rapid and sensitive detection of various chemical and biological analytes, including a record-breaking detection scheme targeting the common foodborne pathogens Salmonella Typhimurium and E.coli.

COLL 577

Surface chemistry and spectroscopic studies of β-galactosidase-carbon dots conjugate: Its use in biosensing

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Nanoparticles have been conjugated to biological systems for numerous applications such as self-assembly, sensing, imaging, and therapy. Development of more reliable and robust biosensors that exhibit high response rate, increased detection limit, and
enriched useful lifetime is in high demand. We developed a sensing platform by the conjugation of β-galactosidase with a gel-like carbon dots (CDs) having high luminescence, photostability, and easy surface functionalization. We found that the conjugated enzyme exhibited higher stability towards temperature and pH changes in comparison to the native enzyme. This enriched property of enzyme was distinctly used to develop a stable, reliable, robust biosensor with increased detection limit. Further, we used Langmuir monolayer technique to understand the surface properties of the conjugated enzyme. It was found that the conjugate was highly stable at air-subphase interface, which additionally reinforces the suitability of the use of the conjugated enzyme for the biosensing applications.

COLL 578

Electronic and optical properties of (4,8) boron-group V nanosheets

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The ascendancy of ultrathin films has emerged as a boon for 21st century nanotechnologies that rely on flexibility, tunable properties, and active surface area. We explore uncharted configurations with (4,8) lattice tessellations that exhibit exceptional light–matter interactions. We find that planar monolayers of boron-pnictogen binary materials possess strong interband absorbance and absorption coefficients that rival existing ultrathin films. These observables were found to occur in the ultraviolet for the boron-nitride nanosheet and in the infrared region of the electromagnetic spectrum for heavier pnictogens, suggesting a route for photocapture of high density solar photons. Moreover, we find the buckled boron arsenide supports a similar, yet slightly decreased, optical response that is blue-shifted from its planar configuration. The strong optical response of these ultrathin films emerges from their unique band structures, localization of π-electrons in the ground state, Van Hove singularities at band extrema, and complementary elemental properties. Consequently, the (4,8) motif demonstrates that many 2D films with distinctly different lattice tessellations from that of established ultrathin materials could have a significant impact on the field.

COLL 579

Submicron surface-plasmon-polariton perovskite laser

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Surface plasmon polaritons (SPP), which squeeze light at nanoscale, offer a new avenue to build sub-wavelength lasers. However, room-temperature SPP lasing especially in the blue-green region has been challenging due to strong metallic absorption. Here, we present room-temperature lasing at 535 nm from hybrid SPP confined in submicron dimension. To compensate for metallic loss, we employed high-gain lead halide perovskite (LHP) cuboid crystals as a gain medium and a 1.4-nm-thick alkanethiol layer coated on gold substrates (Fig A). We synthesized high quality all inorganic lead halide perovskite (CsPbBr$_3$) having micron- and submicron-size using recently developed sonochemical synthesis. Self-assembled monolayers (SAMs) of alkanethiols were prepared by immersing a gold substrate into a solution of the desired thiol. The smallest SPP laser we observed is 830 nm in width and 500 nm in height. Both the LHP crystals and lipid insulators are self-assembled, ensuring atomically flat interfaces with low scattering loss and strong SPP confinement. The lasing SPP mode was measured to have a high group index of 22 and a high Q-factor of 200. The lasing threshold for nanosecond pumping was 11.6 mJ/cm$^2$. The laser linewidth was 0.5 nm near at the lasing threshold. We also present finite-difference time-domain simulation corroborating the experimental results.

![Figure A. Schematic of a CsPbBr$_3$ cuboid-lipid-gold SPP laser and SEM image of a sample B. Output spectra from a 830 nm sized CsPbBr$_3$ cuboid-lipid-gold structure. Inset: Wide-field fluorescence image of the structure above lasing threshold.](image)

**Figure**. A. Schematic of a CsPbBr$_3$ cuboid-lipid-gold SPP laser and SEM image of a sample B. Output spectra from a 830 nm sized CsPbBr$_3$ cuboid-lipid-gold structure. Inset: Wide-field fluorescence image of the structure above lasing threshold.

**COLL 580**

*Hybrid nanocluster-catalyzed, one-pot, mild, and unprecedented stereoselective synthetic route to functional silanes and germanes*
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Metal nanoparticles exhibit unusual chemical and physical properties and have potential to serve as hybrid catalysts. Our laboratory has been exploring the synthesis and utilization of nanocluster catalysts to combine the advantages features of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis. Functionalized germylalkenes, and germylalkanes have application in organic synthesis and materials chemistry but synthetic routes to such synthons have not been fully explored. Metal catalyzed hydrogermylation reactions can produce such synthons but very limited number of reports have appeared in literature. Moreover, in limited examples available, most of the reactions afford mixture of possible isomers and are carried out with activated hydrogermanes or alkynes. To the best of knowledge, systematic studies of metal catalyzed hydrogermylation reactions of functional alkynes are not known.

In this communication, we disclose first example of Pt-nanocluster catalyzed, mild, one pot, high yielding, stereoselective hydrogermylation reaction. In addition, we also present preliminary studies of the nature of recyclable nanocluster catalysts during the catalysis.

COLL 581

Self-Assembled Monolayer Field-Effect Transistors (SAMFETs) and their application in organic integrated circuits

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Organic molecules enable the fabrication of large-area and flexible electronics with low energy consumption. In organic field-effect transistors (FETs), the charge transport mainly occurs in the first few nanometers of the semiconductor at the dielectric-organic interface.

Herein, we present the method of self-assembled monolayers (SAMs) as functional layers in FETs, which combine dielectric and semi-conductive properties in one molecular layer with full control of surface coverage and high reliability in layer formation from solution. We will show newly designed organic molecules with specific anchor groups and molecular design as a tool box for p- and n-type self-assembled monolayer field-effect transistors (SAMFETs). We will demonstrate SAMFET devices based on small molecules and oligomer motifs. Additionally we will provide an integration concept, what enable the fabrication of organic complementary FETs as well as the realization of integrated circuits based on SAMFETs.

COLL 582

Bulk assembly of metal halide clusters and their tunable photophysical properties
Organic-inorganic metal halide hybrids, consisting of a great variety of inorganic metal halide anions and organic cations, are an emerging class of functional crystalline materials with exceptional structural tunability. The family of organic-inorganic metal halide hybrids has been expanded from connected 3D networks to 2D layers, 1D wires and tubes, 0D mononuclear molecules, and 0D molecular clusters. Efficient luminescence was achieved in 0D metal halide clusters with high quantum yield and large Stokes shift. Synthetic control was also realized to demonstrate the relationship between their properties and crystal structures. These findings pave a new way of controlling the photophysical properties in bulk assembly of metal halide clusters.

**COLL 583**

**Engineering supraparticle assemblies**

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Enzymes are potent catalysts with high selectivity and specificity but are subject to instability due to temperature, hydrolytic activity by other enzymes, and reactive oxygen species. These drawbacks severely impede their utilization leading to a need for facile and effective immobilization techniques. Advancement in the synthesis of nanoparticles (NPs) with tunable size, controlled shape, and surface functionalization provides an excellent support for proteins. In this work hybrid supraparticles (SPs), self-assembled superstructures composed of proteins and inorganic nanoparticles, are formed as a tool for the encapsulation and immobilization of proteins, successfully separating them from the environments. SPs are formed by counterbalancing the underlying electrostatic repulsion and attractive interactions of proteins and NPs in the system. Here we show the spontaneous formation of five variations of hybrid SPs, self-assembled from proteins and NPs of various shapes. Iron disulfide (FeS₂) NPs stabilized with thioglycolic acid (TGA), and zinc oxide (ZnO) NPs of various shapes (plates, spheres, and pyramids) were combined with protease, while cadmium telluride (CdTe) NPs stabilized with 2-(dimethylamino) ethanethiol (DMAET) were assembled with two proteins, cytochrome C (CytC) and formate dehydrogenase (FADH). A prominent feature of this work is to
highlight the versatility of forming hybrid SPs, their stability in various environments, and potential application as a new class of nano-tools for a range of applications, specifically encapsulation. Experimental results show iron disulfide SPs are capable of encapsulating and releasing protein with no change in enzymatic activity. The properties of these newly fabricated SP assemblies make them an attractive tool to potentially aid in the development and understanding of complex biological systems.

COLL 584

Surface modification of core/shell quantum dots enables dynamic visualization of neuronal membrane proteins implicated in mental illness

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Core/shell quantum dots have size tunable absorption and narrow emission spectra, are bright, and resistant to photobleaching. With appropriate bioconjugation these quantum dots enable continuous visualization of both membrane protein mobility and protein internalization. This talk will present various bioconjugation strategies as well as findings from dynamic tracking studies of the serotonin transporter protein and the dopamine transporter protein.

COLL 585

Assessment of binding avidity and adhesion forces by multivalent dendrimer nanoprobes

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Multivalent ligand-receptor interactions constitute one of fundamental concepts underlying the design of multifunctional nanoparticles (NPs) in targeted drug delivery. This multivalent effect is not only responsible for high binding avidity but also proposed to confer a strong force of NP adhesion by which NPs remain bound tightly under a shear flow. Despite such significance, the correlation between avidity constants and adhesion forces remains poorly investigated, in part, due to the paucity of well-defined NP probes.

Here we report multivalent dendrimer probes designed as tumor or bacteria-targeted NPs, and discuss two biophysical methods employed to investigate avidity-adhesion force distributions on model surfaces. These probes were designed by conjugating a ligand molecule to generation 5 (G5) PAMAM dendrimer, yielding G5(Ligand)$_n$ ($n =$ mean valency). Each multivalent probe was investigated for its binding avidity to a model cell surface by surface plasmon resonance (SPR) spectroscopy. The same dendrimer conjugate was then used as an atomic force microscopy (AFM) probe to
determine its physical force of adhesion to a model cell surface by single molecule force microscopy. We discuss the distribution of SPR avidity constants and corresponding AFM adhesion forces in response to ligand valency. In summary, this paper reports advances made in the design and biophysical characterization of multivalent dendrimer nanoprobes by SPR and AFM.

COLL 586

Zwitterionic multidentate polymer coating for non-fouling quantum dots

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Nanomaterials with zwitterionic surfaces exhibit exceptional resistance to nonspecific binding of proteins and cells, but zwitterionic coatings for quantum dots (QDs) have not yet been widely explored. We designed new zwitterionic multidentate polymer ligands to produce colloidally stable, homogeneous, compact and non-fouling QDs with efficient conjugation to biomolecules. We modulated the structures of hydrophilic domains of these polymers surface by tuning linker lengths and chemistry, focusing on zwitterion groups such as lysine (lys) and oligo(ethylene glycol) (OEG) (Fig. 1a). In all cases, gel chromatography showed that the coated QDs were similar in hydrodynamic diameter (Fig. 1b). We directly compared the performance of these QDs in resisting nonspecific binding to globular proteins and cells using fluorescence correlation spectroscopy, flow cytometry, and fluorescence microscopy. We surprisingly discovered that QDs with a 1:1 combination lysine and OEG outperformed all others, including lysine or OEG alone. Furthermore, lysine residues allow facile conjugation with amine reactive biomolecules (Fig. 1d). We anticipate that these outcomes can help improve the use of zwitterionic coatings for QDs by further eliminating nonspecific binding in biomolecular imaging and detection applications.
Short-wave infrared quantum dots with compact sizes for microscopic molecular imaging in cells and tissues

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Short-wave infrared quantum dots (SWIR-QDs) have recently emerged as promising fluorescent contrast agent for bio-imaging applications, particularly for \textit{in vivo} animal imaging. The reduced light scattering and reduced autofluorescence in the second infrared window provide increased sensitivity of detection and higher spatial resolution compared with imaging in the visible and first infrared window. Unlike organic dyes with SWIR emission, SWIR-QDs provide higher photostability and quantum yield, however SWIR-QDs composed of Ag\textsubscript{2}S and In\textsubscript{As} often have large physical sizes and lower quantum yield than QDs in the visible spectrum. We have developed a new class of...
QDs with emission tunable from 530 nm to 1500 nm with compact size, high quantum yield, and high photostability. Synthesis begins with conventional CdSe QDs, followed by cation exchange to produce Hg\textsubscript{x}Cd\textsubscript{1-x}Se to shift the band edge absorption to the infrared. A shell of Hg\textsubscript{x}Cd\textsubscript{1-x}S/Cd\textsubscript{x}Zn\textsubscript{1-x}S is then grown layer-by-layer to boost quantum yield, photostability, and further tune emission wavelength. The emission wavelength is then dictated by the final ratio of Hg to Cd. Importantly, the total size is identical across the full range of wavelengths to allow precise multispectral studies in biological media as well as multiplexing across a very wide range of emission. The synthesis protocol also allows tuning of the size independently of the emission wavelength, which adds an extra degree of freedom to select a size threshold on demand for particular biological studies. Further, we combined these materials with new classes of coatings and biomolecular conjugation techniques to explore tissue imaging applications in the SWIR. We find that reduction of autofluorescence can be substantially enabling toward increasing signal-to-noise ratio compared with QD imaging in the visible and first infrared windows.

**COLL 588**

**Ring DNA-carbon nanotube conjugates**

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DNA-single walled carbon nanotube (SWNT) conjugates are emerging nanomaterials for the development of optical probes for imaging biological analytes. Our most recent collaborative research has proposed that short single stranded DNA-SWNT sensors are highly sensitive to minute concentrations of neuromodulators such as dopamine and norepinephrine. We present a computational study of self-assembly of short DNA polymers around SWNT. The replica exchange molecular dynamics (REMD) technique is employed to perform free energy calculations. The free energy landscape of short DNA structures around SWNT reveals the self-assembly of a ring DNA structure around the SWNT, in contrast to the formation of a helical DNA structure around SWNT suggested by prior experimental and theoretical studies. The ring structure of DNA occupies one of the global minima in the free energy landscape, while other global minima are occupied by helical structures. Additionally, experiments show that the putative ring DNA conformation formed by short DNA structures leads to suppression of SWNT baseline fluorescence of ring DNA-SWNT hybrids, as opposed to the relatively high SWNT fluorescence of DNA-SWNT hybrids with conventional helical DNA conformations. We hypothesize that the ring and helical conformations of DNA wrapping
SWNT strongly modulates the relaxation pathway of excitons in DNA-SWNT hybrids, which we exploit for applications in imaging neuromodulation.

COLL 589

**Computational design of nanoparticles with tunable water-mediated interactions**

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Functionalized, monolayer-protected nanoparticles (NPs) are versatile materials with surface properties that depend on monolayer composition. Ultrasmall gold NPs (<10 nms in diameter) are of particular interest for drug delivery applications because their small size enables unique interactions with serum proteins and the cell membrane. However, structure-property-interaction relationships correlating NP compositions with their biological interactions remain unclear and can be challenging to determine experimentally.

Here, we present molecular simulation approaches from our group that can guide the design of NP monolayer compositions for biomedical applications. Motivated by prior work that identified NP hydrophobicity as a key parameter driving cellular internalization and protein adsorption, we use atomistic molecular dynamics simulations to quantify NP hydrophobicity as a function of monolayer physical and chemical properties. These results demonstrate how the cooperative interactions of collections of surface-grafted molecules contribute to spatially varying hydrophobic interactions with homogeneous monolayers. We further show that hydrophobic interactions at uniformly nonpolar interfaces can vary in magnitude depending on the fluctuations of surface-grafted alkanethiol ligands, and that these same fluctuations depend on NP core size and shape. These results are further confirmed by atomic force microscopy experiments. Finally, we present a new deep learning methodology to rapidly screen the hydrophobicity of NPs as a function of monolayer composition using only minimal simulation input. This mechanistic insight and new computational tools can be leveraged to design NPs with desired surface properties.

COLL 590

**Lipase-catalyzed enzymatic biodegradation of carbon dots follow sequential oxidation pathways**

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Carbon dots (CDs) have garnered significant recent attention owing to their excellent luminescence properties, thereby demonstrating a variety of applications for in vitro and in vivo imaging. Understanding the long-term metabolic fate of these agents in a
biological environment is the focus of this work. Here we show that the CDs undergo peroxide catalyzed degradation in presence of lipase. Our results indicate that differently charged CD species exhibit unique degradation kinetics upon being subjected to enzyme oxidation. Further, this decomposition correlates with the relative accessibility of the enzymatic molecule. Using multiple physico-chemical characterizations and molecular modeling, we confirmed the interaction of passivating surface abundant molecules with the enzyme. Finally, we have identified hydroxymethyl furfural as a metabolic byproduct of CDs used here. Our results indicate the possibility and a likely mechanism for complete CD degradation in living systems that can pave the way for a variety of biomedical applications.

Scheme 1. Lipase-Catalyzed Biotransformation of Carbon Dots. Enzymatic Biodegradation in Presence of H$_2$O$_2$Follows Sequential Oxidative Pathway where Intermediates are Identified Using MALDI-TOF Spectroscopy.

**COLL 591**

**Engineering of safe nanocapsules for targeted antibacterial applications**

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The emergence of antibiotic resistance has raised the need for engineering novel highly effective antibacterials with reduced toxicity and lower selection for resistant bacterial
strains. Targeted drug delivery nanosystems hold significant promise to improve the efficacy of the existing antimicrobials and advance the treatment of severe bacterial infections, lowering the risk of resistance occurrence. In this work, we aimed to develop antibacterial nanocapsules (NCs) decorated with targeting ligands for driving with high specificity the therapeutic cargo to the target \textit{S. aureus} pathogen. Oregano oil loaded NCs with size of 195 nm, low polydispersity index and broad spectrum antibacterial activity were produced via a self-assembling nanoencapsulation technology based on biocompatible natural polymers. Layer-by-layer assembly of hyaluronic acid and aminocellulose biopolymers was further performed to introduce surface anchoring motifs for covalent grafting of specific for \textit{S. aureus} antibody, as well as to improve the stability, biocompatibility and release profiles of the designed antibacterial oil-loaded NCs. The grafting of the selected antibody increased the NCs bactericidal efficacy against \textit{S. aureus} by 2 logs. Furthermore, the targeting selectivity of the bactericidal NCs was confirmed via incubation with a mixed inoculum containing Gram-negative \textit{P. aeruginosa} and \textit{E.coli}. The formulated \textit{S. aureus}-targeting NCs selectively reduced the growth of \textit{S. aureus}, but did not affect the normal growth of non-targeted bacteria. Coating the antibacterial NCs with biocompatible polymers and subsequent grafting of the pathogen specific antibody through the available amino groups increased the compatibility of the oil-loaded NCs to human cells and reduced their side effects.

**COLL 592**

**Functionalization of gold nanoparticles for generation of drug and nucleic acid delivery nanoplatforms**

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The unique physicochemical and optical properties of gold nanoparticles (Au NPs), together with their excellent biocompatibility recommend these nanomaterials as a versatile platform technology for delivery of drugs and nucleic acids. We will present our recent results towards the design of ligands that can modulate the surface charge of gold nanoparticles without altering their colloidal stability and thus allow them to act as nucleic acid delivery systems. Alternatively, the design of Au NPs ligands against epitopes expressed on cells in pathological states, as well as Au NPs ligand-drug conjugates can transform Au NPs into targeted drug delivery systems for cancer treatment. The talk will present ligand design details, optimization of AuNPs surface decoration for enhanced colloidal stability, targeting, drug loading and controlled release of cargo. Relevant biological data supporting each application will also be presented.

**COLL 593**
Chemically resolving metal-supported regioisomeric assemblies at nanoscale by ultra-high vacuum, tip-enhanced Raman spectroscopy: Conformation & interaction

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The characterization of surface adsorbed molecules has an immense importance in the field of heterogeneous catalysis, biosensing, miniaturization of electronic devices and fabrication of 2D materials. Only Scanning Tunneling Microscopy (STM) has been lacking to produce the complete chemical information of the molecules adsorbed on the surface. Tip-Enhanced Raman Spectroscopy (TERS) immerges as an upgraded technique and it bridges the topographic images provided by STM and chemical information provided by Raman Spectroscopy. Herein, we demonstrate the structural and chemical analysis of two Porphodilactone regioisomers by UHV-STM, UHV-TERS on Ag(100), Au(100) and Cu(100). Four different laser sources (515nm, 561nm, 594nm, 633nm) have been used to probe their vibrational finger-prints. The study reveals their adsorption geometries on different surfaces and interrogation of different electronic excited states by different laser sources. Even though they are isomer, switching the lactone moiety would cause a significant change in their electronic structure. Furthermore, we can preciously distinguish these two coexisting regiosomeric molecular islands on Ag (100) by vibrational modes imaging (TERS Mapping) with spatial resolution ~0.8 nm. This level of sensitivity could allow us to preciously monitor the molecule-molecule & molecule-substrate interaction at nanoscale.

COLL 594

Amusements with salt-water oscillator

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The study of oscillatory transport phenomena in the far from equilibrium region is important from the point of view of biology and also from the point of view of understanding the nature of instabilities. It is almost certain that living state is a non-equilibrium state in the far from equilibrium region; the further we are from equilibrium the closer we are to life. In the far from equilibrium region one can come across the exotic oscillatory phenomena. The interest of this region is mainly because, most of the physiological process relevant to life occur in this region. Schrodinger has rightly pointed out life is a non-equilibrium phenomena. It is this consideration which makes the investigation in the far from equilibrium region relevant to the physics of living state. There are not many nonlinear systems, which can be chosen to explore this far from equilibrium region. In the chemical reaction system B-Z reaction system is well known. In the field of membrane transport and interface science, Teorell membrane oscillator is the well-studied example. Hydrodynamic oscillator is the simplest device known which can be utilized for exploring the physics of far from equilibrium region. The studies on
The hydrodynamic oscillator are directed toward this ultimate objective. The electrical potential oscillations observed recently in the hydrodynamic oscillator have been investigated. The data suggest that the electrical potential oscillations may be due to oscillating streaming potentials.
Changes in protein’s secondary structure as a result of its interaction with a gold surface

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Proteins are natural polymers which under physiological conditions fold into complex three-dimensional structures. The sequence of amino acids determines the primary structure, the arrangement of fragments of the amino acid chains into α-helices or β-sheets represent the secondary structure elements of a protein. A three-dimensional structure of a protein is known as a tertiary structure. Under pathological conditions, some proteins undergo irreversible changes in their secondary and tertiary structure. In this work, we investigate the adsorption process of a model protein: lysozyme on the gold surface from electrolyte solutions of different pH and ionic strengths. Multi-Parameter Surface Plasmon Resonance (MP-SPR) and Quartz Crystal Microbalance (QCM-D) results show that the maximum adsorption efficiency was obtained at the pH=10, which corresponds to lysozyme’s isoelectric point. Results of MP-SPR and QCM-D methods allow for the calculation of the hydration level of lysozyme’s layer. Amide I’ mode of proteins is of great analytical importance because it provides information on the secondary structure elements of a protein. The conformation of adsorbed on the gold surface lysozyme was examined using Polarization-Modulation Infrared Reflection Absorption-Spectroscopy (PM-IRRAS). The analysis of the amide I’ mode region of the PM-IRRAS spectra shows that the secondary structure of the adsorbed protein differs from the conformation found in the solution phase (examined by CD). Furthermore, we investigated the impact of the surface charge density on the gold electrode on the adsorption process of lysozyme. To modulate the surface charge density of the gold surface electrochemical control was used. The structure of the adsorbed protein depends on both the surface charge density and pH of the electrolyte solution. Most substantial structural changes are observed when lysozyme adsorbs on the positively charged surface from acidic (pH=4) as well as on negatively charged surface from basic (pH=9) condition. The electrostatic attraction determines not only the amount but also the conformation of the adsorbed protein.

Genomic DNA functionalized 3D printed architected materials for drug capture

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Since the discovery of chemotherapy in the beginning of the 20th century, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor via transarterial chemoembolization, or other similar procedures. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized due to the difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Here, we report the fabrication of DNA functionalized 3D printed porous materials that can be used to capture doxorubicin, a commonly used DNA-targeting chemotherapy agent. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of functionalizing the surface with cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. We characterize the surface of the structure and verify the binding of DNA to the surface via XPS, EDS and the use of chemical assays. The efficacy of these functionalized materials were demonstrated in PBS, where we observed a >70% reduction in doxorubicin concentration over a period of 10 minutes, highlighting the viability of this as a method of drug capture.
Dox binding test

Change in doxorubicin concentration over time

COLL 597

Substituent effects on the organization of methacrylate monomers and existing intermolecular interactions at air-liquid interface using sum frequency generation spectroscopy

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Investigation of monomer conformations at the air-liquid interface is important as it provides 1) insight to the relationship between surface structure and the properties of monomers, 2) a basis for detecting trace residual monomers on a surface of a polymer matrix which is a measure of the toxicity of a polymer material. Methacrylate-based monomers and their polymers are important because of their applications in the biomedical field, adhesives, and lubricant coatings. The assessment of conformational differences in functionalized monomers assists in designing polymers for effective
polymer thin films. In this work, the ethyl end of the methacrylate backbone is substituted with cyano (-CN), hydroxy (-OH), chloride (-Cl), bromide (-Br), iodide (-I), and carboxy (-COOH) groups to investigate the electronic effect of the substituents. These functionalized monomers are synthesized by the nucleophilic addition/elimination reaction between methacryloyl chloride and the substituted alcohol. Then these pure monomers are characterized using sum frequency generation (SFG) spectroscopy at the air-liquid interface. The substituents affect the orientation of the molecular groups at the interface. The average tilt angles of the α-methyl group of -CN, -OH, -Cl, and -Br substituted monomers are 40.0°, 54.6°, 55.1°, and 58.7°, respectively. When the α-methyl group is tilted at an angle closer to the surface normal, the C=O stretching mode at ~1725 cm⁻¹ is intensified (-CN substituted monomer) suggesting that the C=O molecular group is also orienting closer to the surface normal. When the α-methyl group is tilted at an angle closer to the surface, the C=O stretching mode is diminished (-Br substituted monomer), suggesting that the C=O group is orienting further away from the surface normal. The apparent intensity variation of the C=O stretching mode could possibly be governed by surface inductive effects triggered by the substituents affecting the overall interfacial monomer conformations.

**COLL 598**

**Parallel orientation to the interface: Surface chemistry and spectroscopic study of α-synuclein and the NAC part**

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α-Synuclein (α-syn), a protein contains 140 amino acid residues, is the major protein component of Lewy bodies which is the hallmark deposition in the dying dopaminergic neurons in the brain of Parkinson’s disease patients. The primary structure of α-syn constitutes three domains: N-terminal residues 1–60; the nonamyloid component (NAC) which spans residues 61–95 and is responsible for the aggregation; and residues 96–140 which comprise the negatively charged C-terminus. Despite the abundance (~ 1 % among the total proteins) in the brain, α-syn accumulates in the presynaptic terminals where exists high concentration of amphiphilic structure (e.g., liposomes and cell membrane) and the reason of the accumulation is not clear. Here, both α-syn and its NAC part (i.e., α-syn(61-95)) were synthesized and purified. α-Syn and α-syn(61-95) were shown to be able to form a stable Langmuir monolayer at the air-water interface, which has been widely used to mimic the amphiphilic structure in vivo. From circular dichroism results, both α-syn and α-syn(61-95) transform from unstructured conformation in aqueous solution to α-helix at the interface. In addition, surface FTIR techniques have shown a parallel orientation of the axis of the α-helix of both α-syn and α-syn(61-95) to the interface. Due to the high stability at the interface, no aggregation of α-syn(61-95) or α-syn has been detected.

**COLL 599**
Semiconducting block copolymer thin films via surface-initiated polymerization

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Surface-initiated Kumada catalyst-transfer polymerization (SI-KCTP) is becoming a promising method to prepare semiconducting polymer thin films for cutting-edge applications, such as ITO-free photovoltaic devices, as it can deliver polymer films with superior chemical and mechanical properties. Despite the possibility to use SI-KCTP to prepare complex architectures and mesoscale structured thin films, to date, primary developments have been focused on simple homopolymer films. In this presentation, we will describe a new SI-KCTP based approach toward all-conjugated diblock copolymer thin films. We prepared thin films of polythiophene-\(b\)-poly(\(p\)-phenylene) on various substrates. The films displayed properties remarkably different from the properties of the constituent homopolymer films. They have been characterized using a variety of methods such as UV/vis and fluorescence spectroscopy, cyclic voltammetry, XPS, surface microscopy, X-ray scattering, and neutron reflectivity. This new approach towards all-conjugated diblock copolymer thin films can offer a new materials platform for various applications.

3D structure fabrication using 2D controlled wetting surfaces
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3D micro-structure fabrication has attracted interest for both for fundamental issues as well as applications that include as micro-lenses for light collection and micro-droplet arrays for micro-bioassay. Previously reported methods require a fabricated 3D mold, a pulsed laser system, or photolithography protocols for individual substrates. We present a novel 3D structure fabrication technique using 2D hydrophilic / hydrophobic patterned wetting surfaces. The preparation of controlled wetting surfaces and subsequent liquid coating processes create reproducible sessile droplet arrays. These arrays can be covered with controlled thickness silicone prepolymer that are catalytically cured. The droplet array serves as a mold and the liquid is retained in the more hydrophilic regions due to a hydrophilic / hydrophobic confinement effect. The velocity of liquid appplication affects the volume of coated liquid yielding molds with varying feature height. Several types of liquid, including ionic liquids, water and solutions were studied to confirm the versatility of this molding process. Immiscibility between the silicone and certain ionic liquids permitted precise molding. On the other hand, the shape of resulting molded silicones when water was used depended on relative humidity, because of the significant water vapor permeability of silicones. In this talk, we will present our work on the preparation of wetting controlled surfaces, the creation and effect of the liquid droplet as a mold, and subsequent molding processes.
Controlled wetting surfaces and subsequent liquid coating processes

**COLL 601**

*Operando* PM-IRAS+Raman spectroscopy for elucidating surface poisoning mechanisms of Pd-based hydrogen separation membranes in complex reaction mixtures

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Palladium-based membranes are attractive for hydrogen separation applications, such as membrane reactors, due to their rare combination of high permeability and high selectivity for hydrogen separation from mixed gas streams. Their near-infinite selectivity for hydrogen separation results from the unique hydrogen transport mechanism. Molecular H\(_2\) dissociatively adsorbs on the catalytically active surface of the membrane, producing H atoms which diffuse through the bulk metal lattice, and recombine on the downstream surface. Only H atoms can diffuse through the membrane so selectivity over other gases is essentially infinite. However, other gases that are common in hydrogen-containing gas streams, such as CO, propylene and H\(_2\)S, can severely poison Pd-based membranes and inhibit hydrogen transport. Development of membranes that resist poisoning is hindered by a lack of a fundamental understanding of how these reactive gases inhibit hydrogen transport. More specifically, it is not clear: (1) what compounds are formed when these gases react with Pd-based membranes, (2) where these compounds are located (surface versus bulk), (3) how these compounds inhibit hydrogen transport (catalytic surface poisoning versus slowing bulk H atom diffusion), or (4) how the Pd-alloy composition influences (1) through (3). This lack of fundamental understanding is due in part to the lack of commercially-available tools that are capable of monitoring the evolution of the membrane structure *in-situ* under realistic permeation conditions. To address this problem, our group is developing a multi-mode *operando* spectroscopy instrument to provide new scientific insights into membrane poisoning mechanisms. This instrument uses both polarization-modulation infrared-reflection absorption spectroscopy (PM-IRAS) and Raman spectroscopy to interrogate the membrane composition *in-situ* under realistic permeation conditions while trans-membrane hydrogen permeation rates are measured simultaneously. Thus, this technique can correlate microscopic surface processes to macroscopic permeation rates and elucidate membrane poisoning mechanisms in more detail than is possible with *ex-situ* techniques. In this talk, I will demonstrate how this tool can elucidate poisoning mechanisms of Pd, Pd-Cu, and Pd-Ag alloy membranes in great detail, by correlating inhibition of hydrogen transport to CO adsorbed on specific sites on the membrane surface.

**COLL 602**
SuFEx-based hydrolysis strategy for the preparation of sulfate cation exchange resins

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A sulfate cation exchange resin was fabricated based on an unexpected SuFEx hydrolysis by treatment with tert-butyldimethylsilyl (TBS) protected alkyl alcohol and catalyst. The polystyrene-based beads in various degrees of fluorosulfonation were synthesized by the emulsion/suspension polymerization of styrene and 4-vinylphenyl sulfofluoridate with divinyl benzene as a crosslinker, followed by the hydrolysis in strong basic solution and mild SuFEx-based hydrolysis condition. Then, FTIR was used to probe the presence of sulfate moieties on the beads after hydrolysis. The varying sulfate densities were investigated by zeta-potential. The results indicated this strategy has a good control over the charge density on ion exchange resins. Compared to strong basic hydrolysis, the hydrolyzed beads with milder SuFEx-based treatment can keep an intact spherical structure revealed by scanning electron microscope (SEM). Finally, a simple ion capture experiment was performed employing a cationic dye, methylene blue, to evaluate the ability of these hydrolyzed polymeric products to serve as ion exchange resins. It was found that the amount of color retained by the new cation exchange resins qualitatively appeared to correlate well with the density of sulfate moieties present as polymer beads.

COLL 603

Facile grafting of zwitterions on membrane surface using bio-inspired polydopamine

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Water membranes usually suffer from surface fouling, which dramatically decreases water permeance. The fouling is often mitigated by hydrophilizing the membrane surface, such as coating by hydrophilic zwitterions (ZWs) and poly(ethylene glycols) (PEGs). We demonstrate a facile method to graft the ZWs and PEGs onto the membrane surface by co-depositing with dopamine. Dopamine can be easily polymerized to polydopamine (PDA), which can covalently bind ZWs or PEGs containing acrylate or amine functional groups through Michael Addition. Specifically, acrylate-terminated compounds include sulfobetaine methacrylate (SBMA) and PEG-diacylate (PEGDA), and amine-terminated SB-amine and PEG-diamine were co-deposited with dopamine onto the silicon wafers and ultrafiltration (UF) membranes. The effect of the composition of coating solutions and coating time on the coating layer thickness, compositions, and hydrophilicity are investigated. The coating can deposit a layer of 10 – 50 nm containing 30 – 72% ZW or PEG. The effect of coating and surface
chemistry on the membrane properties (including molecular weight cut-off and water permeance) will be systematically investigated to derive the structure/property relationship.

COLL 604

**Janus-type MnOx-AgI nanoparticles as self-sensitized oxygen-evolving catalysts**

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Janus nanoparticles (NPs) integrating two chemically distinct materials are of great significance in nanocatalysis in terms of harnessing catalytic synergies that are not exist in either component. We present a new and robust method to prepare Janus-type MnOₓ-AgI NPs using an oxidative nucleation and growth method; and we demonstrate their catalytic synergies as self-sensitized photocatalysts for solar-driven water oxidation. MnO octahedrons prepared through thermal decomposition of Mn(oleate)₂ are used as seeds first to grow highly monodispersed Janus MnOₓ-Ag I NPs. Followed by a mild iodination of MnOₓ-Ag NPs with CH₃I at room temperature, well-defined Janus MnOₓ-AgI NPs can be prepared in remarkable yield and high homogeneity. Compared to KI and I₂ as reported in previous literatures, the iodination using CH₃I is non-disruptive to the nanostructures of Ag and this leads to the formation of spherical core-shell Ag@AgI (about 42 % iodination yield) as a light-harvesting antenna in as-resultant MnOₓ-AgI NPs. The oxidation of MnO was observed to form mixed amorphous n-type MnOₓ in the course of the growth of Ag domains and the formation of AgI domains.
Janus MnO$_x$-AgI NPs therefore integrated $n$-type MnO$_x$ with $p$-type AgI together as a self-sensitized photocatalytic WOR catalyst. Janus MnO$_x$-AgI NPs show a superior photocatalytic activity (358 mmol O$_2$ per mg catalyst in 4 min) even in the absence of [Ru(bpy)$_3$]$^{2+}$ as a photosensitizer. The marriage of MnO$_x$ and AgI is understood to effectively separate the photoexcited electrons to largely enhance the photocatalytic active, compared to pure MnO$_x$ and AgI.

**COLL 605**

High-pressure nanocrystals: New structures and new optical properties

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High-pressure offers a potential strategy to the synthesis of nanocrystals (NCs) with new phases, and provide new insights into the phase stability in metastable nanocrystals. Also, high pressure enables new phase transition routines and desirable properties of functional nanocrystals. In this regard, a new structure of B31 phase MnS NCs was successfully synthesized from rocksalt MnS NCs via pressure processing treatment. It is particularly worth noting that the generated new structured MnS NCs were captured as expected by quenching the high-pressure phase to the ambient conditions at room temperature. In addition, the metastable phases of both zinc blende and wurtzite MnS NCs would convert to the stable rock salts MnS under high pressure, and phase transition is reversible. We also observed different phase transition routines in WZ-CuGaS$_2$ NCs, YPO$_4$ NCs and YV$_{1-x}$P$_x$O$_4$ NCs. Likewise, obtaining improved performance from nanomaterials at high pressure is important over a wide range of applications. We here demonstrate a pressure-induced emission enhancement (PIEE) of oleic acid capped CdSe NCs. First-principles calculations indicate that the increased Hirshfeld charge transferred from the OA molecule to CdSe NCs, accompanied by the disappearance of surface-related trap states at high pressure, is highly responsible for the marked PIEE.
Sub-50nm ultra-thin hybrid ED membrane made by colloidal self-assembly and plasma-defined atomic layer deposition

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Here we introduce the fabrication of ultra-thin membrane based on colloidal self-assembly and plasma-defined atomic layer deposition. Selectively permeable membranes with high flux and selectivity are important for many applications including water desalination, H\(_2\) purification, CO\(_2\) capture, as well as selective ion transport. Reduced membrane thickness and precise pore size/chemistry control are the keys for achieving combined high flux and selectivity. Compared to membranes in natural biological systems that are typically down to 4 nm in thickness and the pores are precisely constructed by molecular assembly, synthetic industrial membranes are difficult to be fabricated with similar molecular level precision and are typically 100-1000 times thicker. ALD is a layer-by-layer deposition method that builds up a thin layer with atomic precision in structure and compositions. By combining colloidal self-assembly and a “plasma-defined” ALD process where the location of ALD modification is confined by plasma irradiation, sub-50nm ultra-thin ED membranes have been successfully fabricated. To achieve cation or anion selectivities, functional groups/species such as amine or carboxyl groups have been successful integrated into the hierarchically structured membranes and excellent performances in selective ion transport have been achieved.

**COLL 607**

Architecting nanomaterials for naval applications

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Here, we will present an overview of several projects centered around colloidal nanocrystal (NC) design and synthesis for naval applications. These applications include structural health monitoring, taggants, and corrosion resistance. The first two applications require the design of metallic NCs with a large refractive index (RI)-sensitivity. The tagnant-focused design also leverages tunable plasmonic properties beyond the local environment dependence such as NC size-, shape-, and composition-dependent properties. In both of these designs, we show that new multifunctional platforms are possible with less conventional plasmonic metals. In fact, to the best of our knowledge, these bimetallic NCs display the highest ensemble RIS measurement to date for colloids with LSPR maximum band positions ≤ 900 nm in water. This effect is accounted for by the lower dielectric dispersion at the resonant wavelength, and good agreement is found between experimental findings and simulations of the RIS.
corrosion resistant NC design leveraged recent reports of shape evolution of anisotropic metallic nanocrystals (NCs) during dissolution, which suggested that a new morphology-driven approach may be added to our current corrosion mitigation toolbox. These studies tracked NC morphology changes, using in situ transmission electron microscopy (TEM), and revealed that some colloidal NC shapes are short-lived while others are much longer lived. While the implications of these studies focused on the fundamental insight into NC morphology-stability relationships, we expand those implications to include new strategies to reduce corrosion susceptibility. For example, nanostructures that are resistant to dissolution in highly oxidizing environments may inform the design and selection of corrosion-resistant materials and finishing processes. Currently, there is a lack of morphology-lifetime correlation in corrosive environments for alloy NCs in which selective oxidation becomes a critical factor. Here, we present a mechanistic understanding of nanoscale structural evolution of in corrosive environments for a model bimetallic system utilizing in situ TEM. This mechanistic understanding drove the development of morphology-based design rules to inform the selection of materials that are resilient throughout their lifecycle.

**COLL 608**

**Crystal structure of Au\textsubscript{36}(SPhCH\textsubscript{3})\textsubscript{24} gold nanomolecules**

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Gold nanoparticles (Gold NPs) have a vast range of applications in optics, sensors, gene delivery, bioimaging, targeted drug delivery, catalysis, solar cells etc. As we go down in size to 1-2 nm, gold nanomolecules show molecular like behavior with discrete electronic structure. They have a distinct number of gold atoms protected by specific number of thiolate ligands. Discovery of several Au\textsubscript{36} crystal structures have been reported with different ligands. These compounds can be synthesized in large scale and are remarkably stable; also they can be crystallized easily. In this work, we report the synthesis, characterization, optical properties and the crystal structure of Au\textsubscript{36}(SPhCH\textsubscript{3})\textsubscript{24} nanomolecules and how the ligand affects the properties of the Au\textsubscript{36}(SR)\textsubscript{24} nanomolecules.

**COLL 609**

**Self-assembly of non-spherical nanoparticles into functional supercrystals**

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Nanoparticles are fascinating in many ways. Self-assembly of various building blocks into macroscopic structures with desired features and functions, is an interesting theme that runs through chemistry, biology and material science. In this talk, I will first show our recent progress in the self-assembly of non-spherical nanoparticles including nanocubes, nanorods, and nanodumbbells. The roles of non-spherical nanoparticle shape during this self-assembly behavior are of great interest, and different solvents have been demonstrated to modulate the individual particle interactions to control the final nanoparticle assembly pattern. Additionally, the stability of different nanoparticle superlattice polymorphs has also been provided by delicate solution calorimetric measurements. Last, I will talk about how to use self-assembly technique to prepare ordered Au honeycomb mesoporous nanosheets with plasmonic hotspots.

**COLL 610**

**Electric field-driven assembly of silver nanocrystal superlattices**

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In this talk we describe the use of electric fields to drive nanocrystals assembly into superlattices. First, we demonstrate that field driven assembly can deposit well-ordered superlattices over large (cm²) areas. The process is amenable to wafer-level deposition, reversible and several orders of magnitude faster than conventional solvent evaporation or co-solvent techniques. Beyond creating a nanocrystal flux, we show that the electric field can be used to improve the polydispersity of the solution near the electrode, leading to higher crystalline quality. We use this improvement in crystal quality to probe nanocrystal-substrate interactions and show that the structure of nanocrystal superlattices can be switched from face centered cubic to body centered tetragonal by changing the hydrophobicity of the substrate. Although there have been several studies that show that superlattice structure can be altered by tuning the nanocrystal building block (core plus ligands) or solvent environment, we believe this is the first demonstration showing that superlattice structure can be dictated by the nanocrystal-substrate interaction alone. This adds a new tool for nanocrystal assembly that has not been harnessed before.

**COLL 611**

**Pressure response to the structure and optical properties of metal halide perovskite nanocrystals**

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Metal halide perovskites (MHPs) are of growing interest for their extraordinary performance in optoelectronic devices and solar cells. However, developing an effective strategy to achieve the bandgap engineering of MHPs in order to satisfy the practical
applications remains a great challenge. Herein, we introduce high pressure to tailor the optical and structural properties of MHP-based cesium lead halide nanocrystals (CsPb$_{1-x}$Mn$_x$Cl$_3$ NCs, CsPbBr$_3$ NCs, CsPbI$_3$ NCs, and Cs$_4$PbBr$_6$ NCs). Both the pressure-dependent steady-state photoluminescence and absorption spectra experience a stark discontinuity at the phase transition point. Simultaneous bandgap narrowing and carrier-lifetime prolongation of CsPbBr$_3$ trihalide perovskites NCs were also achieved as expected, which facilitates the broader solar spectrum absorption for photovoltaic applications. First-principles calculation unravels that the bandgap engineering is governed by orbital interactions within inorganic Pb–Br/I frame through the structural modification. Changes of band structures are attributed to the synergistic effect of pressure-induced modulations of Br/I–Pb bond length and Pb–Br/I–Pb bond angle for PbBr$_6$ octahedral framework. Furthermore, the significant distortion of lead–bromide octahedron to accommodate the Jahn-Teller effect at much higher pressure would eventually lead to a direct to indirect bandgap electronic transition. Likewise, The Cs$_4$PbBr$_6$ NCs exhibit an unexpected pressure-induced emission (PIE) at room temperature when the intrinsically nonemitting nanomaterials are compressed to 3.01GPa. Such pressure-induced emission (PIE) may be ascribed to the enhanced optical activity and the increased binding energy of self-trapped excitons upon compression. Our work enables high pressure as a robust tool to control the structure and bandgap of MHPs NCs, thus giving an insight into the microscopic physiochemical mechanism for those compressed MHPs nanosystem.

COLL 612

Measuring the transverse lipid diffusion of peptidolipidic systems using a novel SANS approach

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The plasma membrane is a cell’s first line of defense, protecting and separating important cellular content from harmful external agents. A class of lytic peptides have evolved to destroy this barrier, displaying antimicrobial, antifungal, and antitumor properties. As strains of antibiotic-resistant bacteria continue to arise, these highly conserved peptides can act as templates for the intelligent design of therapeutic agents. A postulated mechanism these peptides can operate upon is the disruption of a vital membrane property: lipid asymmetry - where individual leaflets possess different lipid compositions, imparting unique biophysical and biochemical properties. The cell expends an enormous amount of energy establishing and maintaining this asymmetry; rightly so, as it is involved in physiological functions such as blood clotting and apoptosis. Therefore, a loss of asymmetry can act as a significant source of cell death.

There are studies that claim the presence of flip-flop (where phospholipids translocate to the opposing monolayer) after the introduction of lytic peptides suggests certain pore formation. However, research demonstrating that these pores are the direct cause of phospholipid flip-flop lack reliability because of the membrane-disruptive and interpretative techniques used. For example, fluorescence and electron spin resonance studies rely on labelled lipid probes to monitor flip-flop. The issue is two-folds: the bulkiness of these probes perturb membrane features; and the flip-flop rate measured is not that of native lipids but of chemically and structurally altered lipids.

To help elucidate mechanistic differences between various model antimicrobial peptides, novel and known small angle neutron scattering (SANS) approaches are applied to monitor lipid flip-flop in asymmetric and symmetric large unilamellar vesicles, in peptide-free conditions as well as with gramicidin, melittin, alamethicin and pHLIP. This was made possible due to the neutron contrast difference between individual bilayer leaflets or vesicle populations, depending on approach. Interestingly, our results also reveal the importance the method of peptide incorporation has on bilayer stability, specifically lipid asymmetry, whereby external addition through solvent scrambles the bilayer, whereas preincorporation does not. Herein, we demonstrate a novel use of SANS on more biologically relevant asymmetric model membranes as a means to measure transverse lipid diffusion.

**COLL 613**

**Self-assembly/disassembly of giant double-hydrophilic polymersomes at biologically-relevant pH**

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Double-hydrophilic copolymers containing different hydrophilic blocks can self-assemble to form stable vesicles in aqueous solution despite having no apparent hydrophobic block. Self-assembly of double-hydrophilic copolymers consisting of poly(ethylene oxide) (PEO) and poly(acrylic acid) (PAA) is intriguing because not only is PAA responsive to changes in pH, but also PAA can participate in hydrogen bonding interactions with itself or PEO under appropriate pH conditions. We present a class of pH-sensitive polymer vesicles prepared by the self-assembly of double-hydrophilic PEO–PAA diblock copolymers (Scheme 1). To the best of our knowledge, this is the first work that shows the formation of micron-sized vesicles of PEO–PAA copolymers. We survey the self-assembled morphologies of PEO–PAA copolymers with different PEO fractions and demonstrate substantial degradation of giant polymer vesicles by adjusting solution pH. Furthermore, these vesicles are capable of encapsulating and releasing small molecule cargo. Because the switching behavior of the diblock copolymers occurs at biologically-relevant pH environments (2 to 9), these polymer vesicles have potential biomedical applications as smart delivery vehicles.

Scheme 1 Formation and degradation of PEO–PAA polymer vesicles.

COLL 614

Effect of cholesterol on DOPC lipid membranes

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Cholesterol is an essential component of mammalian cell membranes and is present in varying abundance in different membrane types, from <5 mol% in mitochondrial membranes up to 50 mol% in plasmatic membranes. Functionally, cholesterol is a key molecule in controlling the fluidity, packing state, and the lateral in-plane heterogeneity in lipid bilayers. While it is known that cholesterol has some ordering effects on unsaturated lipids, the effect of cholesterol on the mechanical properties of unsaturated lipid membranes is controversial, leaving open questions about the interaction mechanism between cholesterol and unsaturated lipids. Here, we report neutron spin-echo (NSE) results on cholesterol-enriched mono-unsaturated lipid membranes, specifically DOPC, with cholesterol content of 0 to 50 mol%. NSE directly probes the bending fluctuations of the membranes and allows for direct extraction of the membrane bending rigidity, $\kappa$. Our results show an increasing trend in $\kappa$ with increasing cholesterol content, up to a 3-4 fold increase at 50 mol% chol. These results are in excellent agreement with bending rigidity values obtained from real-space fluctuation analysis from molecular dynamics simulations on cognate DOPC-chol bilayers. The simulations also agree with structural membrane properties obtained from SANS measurements and provide detailed mechanistic insights into cholesterol-DOPC interactions that in turn offer a rationale for the observed trends in the bending rigidity modulus. Based on these findings, we propose an approach to remedy the shortcomings of the polymer-brush model in cholesterol-containing unsaturated lipid membranes. This allows further analysis of NSE data for the calculation of area compressibility moduli of DOPC-chol membranes.

**COLL 615**

**Imaging membrane viscosity through nonlinear light scattering**

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Membrane viscosity, or inversely, membrane fluidity, is a critical physiological property of cells that are relevant to a variety of cellular processes, including: mitigating mechanical stress, controlling diffusion of metabolites and reactive species, monitoring temperature of the local environment, interactions of macromolecules, and a series of cascading molecular signaling mechanisms.

We show that the passive transport rate of a molecule diffusing across a membrane can be used as a measure for quantifying membrane viscosity based on the Stokes-Einstein relation, which stipulates that the local solvent viscosity is inversely proportional to the molecular diffusion constant of the solute. Previously, we have demonstrated that molecular transport across cell membranes can be characterized using Second
harmonic Light Scattering. SHLS applied in the imaging modality can resolve molecular transport rate at a single living cell membrane with subcellular, regional resolution. Here we present the microscopic images of membrane viscosity of Human Dermal Fibroblast cells obtained from SHLS microscopy. The regions of the membranes under high strains display higher membrane viscosity.

COLL 616

Determination of biomembrane elastic properties via analysis of thermal fluctuations of lipid orientation in molecular simulations

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The analysis of lipid director fluctuations in Fourier space is explicitly shown to yield identical results to the analysis of shape fluctuations for the determination of bilayer bending rigidity in large (32,000 MARTINI lipids) simulated membrane systems. Some slight improvements upon previously discussed numerical procedures are needed to fully realize this correspondence; these details will be discussed. The technique also provides lipid tilt and lipid twist moduli. Bilayer elastic properties for a dozen different lipids as obtained from fully-atomistic simulations will be presented.

COLL 617

Interrogating cell membrane organization with secondary ion mass spectrometry

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The plasma membrane of the mammalian cell is organized into domains that have different protein and lipid compositions. The ability to image protein components of interest in cell membranes with high spatial resolution and selectivity has revealed that the functions of some membrane proteins are correlated with their distribution within the membrane. Cholesterol, sphingolipids, and other lipid species are also expected to have non-random distributions within cellular membranes that are required for membrane function. Here we probe this expectation by using a high-resolution secondary ion mass spectrometry (SIMS) approach to image isotope-labeled lipids and proteins of interest in mammalian cell membranes with ≤100-nm-lateral resolution. Our SIMS imaging revealed that sphingolipids are located within micrometer-scale plasma membrane
domains, but cholesterol is evenly distributed on the cell surface. By imaging isotope-labeled cholesterol and sphingolipids in parallel with immunolabeled membrane proteins, we have tested the hypothesis that the influenza virus envelope protein, hemagglutinin, clusters within cholesterol- and sphingolipid-enriched plasma membrane domains. We have also used this approach to directly test the hypothesis that the influenza virus assembles and buds at regions of the plasma membrane that are enriched with cholesterol and sphingolipids.

**COLL 618**

**Transverse lipid organization dictates bending fluctuations in model plasma membranes**

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Bending fluctuation is one of the most important dynamic modes of lipid membranes. These fluctuations play a vital role in many biological processes, most notoriously, contributing to the regulation of membrane protein activity. We investigated the bilayer structural properties and the bending rigidity of liposomes with an asymmetric transbilayer distribution of high- and low-melting lipids (asymmetric large unilamellar vesicles, aLUVs). The aLUVs were generated using cyclodextrin-catalyzed lipid exchange. The resulting aLUVs were composed of an egg sphingomyelin (ESM) enriched outer leaflet and a 1-Palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE) inner leaflet. A combination of small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) were used to determine the bilayer structure at different temperatures. Using neutron spin-echo (NSE) spectroscopy, the aLUVs were measured at three temperature conditions; i) where ESM and POPE are both gel, ii) ESM is gel and POPE is fluid and iii) both ESM and POPE are fluid. Under these conditions we find that the asymmetric organization of lipid increases the overall strength of the bending fluctuations, thus giving direct physical evidence of lipid-driven interleaflet coupling.

**COLL 619**

**Correlated membrane bound protein conformational transitions and lipid dynamics provides new insights into leakage kinetics by pore forming toxins**

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Pore forming toxins are a class of cytotoxic proteins implicated in a wide range of virulent bacterial infections and diseases. These toxins bind to target membranes, undergo oligomerization to form transmembrane pores that eventually lead to cell lysis. While the protein is believed to undergo large conformational changes during assembly and pore formation, the connection between these membrane bound states and lipid reorganization during pore formation is largely unexplored. In this study, we provide a microscopic connection between pore formation, lipid dynamics and leakage kinetics by using a combination of FRET and FCS measurements of listeriolysin O (LLO) on single giant unilamellar vesicles. Upon exposure to LLO, two distinct populations of vesicles with widely different leakage kinetics emerge. We attribute these differences to the existence of an ensemble of oligomeric intermediates, sampling various membrane bound conformational states of the protein, and relate these to concomitant changes in lipid dynamics and leakage. Molecular dynamics simulations capture the influence of membrane bound states of a single monomer on the underlying lipid dynamics and provide molecular insights into various membrane bound states observed in the FRET experiments. Our study provides a microscopic connection between membrane binding, conformational changes and their influence on lipid reorganization which enhances our understanding protein-membrane mediated cell lysis.

COLL 620

Impact of surface potential on plasmonic and electronic properties of metal oxide nanocrystals

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Metal oxide nanocrystals doped with a few percent of aliovalent dopants become electronically conducting and support strong light-matter interactions in the infrared due to localized surface plasmon resonance (LSPR). In the prototypical material, tin-doped indium oxide (Sn:In$_2$O$_3$), we discovered that these properties are strongly affected by the presence of a thin depletion layer at the nanocrystal surface where the free electron concentration is strongly depressed compared to the core of the nanocrystal. Depletion arises due to the pinning of the Fermi level at the surface, which is associated with the presence of surface electronic states within the electronic band gap. The surface potential can also be tuned electrochemically, so we used in situ FTIR spectroelectrochemistry to ascertain the impact of depletion on the dynamically tunable optical spectra. These experiments, carried out for varied diameter nanocrystals with varied dopant concentration, illuminate the physics of depletion effects. Critically, we expect the potential for near-field enhancement of incident light to be significantly hampered, especially for thicker depletion layers (1-2 nm). Depletion layers also present barriers to transporting electrons from one nanocrystal to the next in thin films. As a result, films of even the most highly doped nanocrystals are very poor conductors. Outside the electrochemical cell, the surface states that induce depletion are associated with surface hydroxyl groups. Based on these physical and chemical insights, we have
begun to uncover surface chemical strategies to tune, mitigate, or even eliminate depletion effects and thereby enhance optical and electronic properties.

**COLL 621**

**Surface matters: Interface effects on optoelectronic behavior of semiconductor nanocrystals and hybrid semiconductor-metal nanoparticles**

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The surface of colloidal semiconductor nanocrystals (SC NCs) is of paramount importance dictating their size- and shape-controlled synthesis and affecting their optoelectronic properties. Surface manipulations enable the wet-chemical processability of the NCs. This characteristic, combined with their size, shape and composition tunable properties, has led to emergence of SC NCs as promising materials for diverse applications. However, the NC surface and its ligands layer, still remain under-explored. We will present aspects concerning interfaces in nanocrystals including the nanocrystal inorganic-ligands interface, the nanocrystal ligands layer, and lastly the ligands-solvent interface.

A first aspect will address the role of core/shell interfaces in nanorods, where the use of graded shell composition greatly enhances the optical properties of seeded nanorods. Moving outwards, we will present a study of the size dependent dynamic properties of the ligand shell for core/shell quantum dots (QDs) of different sizes. Our results show that increasing the curvature of the surface (by reducing the radius of the QD), allows the ligands to move more freely within the ligand layer and thus decrease the effective viscosity of the ligand shell. This has been done by attaching organic dye molecules directly to the surface of the QDs and measuring their time dependent photo selection anisotropy. Lastly, we will introduce the effects of the ligands on the photocatalytic performance of hybrid semiconductor-metal nanoparticles.

**COLL 622**

**Cooperative action of hot carrier and surfactant in SPR-driven growth of Au nanostars**

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Surface plasmon resonance (SPR)-mediated synthesis of plasmonic nanostructures has gained intense research interests in recent decades. Herein, we demonstrate the SPR-mediated Au nanostar formation in the presence of surface-adsorbed iodide. Our investigation reveals that the iodide traps hot carriers and facilitates the oxidative etching of Au at high-indexed facets, which eventually results in the anisotropic growth of Au nanostars. Our studies provide a molecular-level view of the mechanism behind
the SPR-mediated formation of Au nanostars and emphasize the importance of ligand-hot carrier interaction in regulating photochemical processes.

COLL 623

**Surface chemistry effects on the ultrafast dynamics of propagating surface plasmon polaritons in metal nanostructures**

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Surface Plasmon Polaritons (SPPs) are coherent electron motions that propagate at metal-dielectric interfaces. The timescales for energy relaxation of these motions are extremely fast and are hard to measure by conventional techniques. In this talk, it will be shown that the dephasing times for the leaky SPP modes of noble metal nanostripes can be measured by combining real-space scattered light microscopy images with Fourier-space (or back focal plane) images. These measurements have been performed for bare nanostripes, and nanostripes coated with semiconductors such as TiO$_2$ or Al$_2$O$_3$, or self-assembled monolayers. Subtracting the results for the bare and coated nanostripes provides information about the SPP dephasing induced by the coating, and generates unique information about the timescales for electron transfer from SPPs to semiconductor or molecule species via the hot-electron generation mechanism. Experiments have also be performed on nanostripes coated with thin films of excitonic species (dye molecules or quantum dots), where hybrid plasmon-exciton states can be created. These measurements show that the coupled states have very different lifetimes compared to the uncoupled states.

COLL 624

**Computational prediction of activation energy without transition state calculation**

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In an effort to reduce the computational expense of transition state calculations, we proposed a simplified model to predict the activation energy barrier without searching transition state. Using frustrated Lewis pairs as example catalyst, we found that the activation energy for C-H bond cleavage in methane is proportional to the geometrical mean value between the catalyst’s HOMO/LUMO gap and the binding energy of the catalyst. The proposed model provides a simplified approach to calculate the activation energy barrier of reactions without time consuming transition states calculations and is worth of expanding to a more general case in the future.

COLL 625

**Plasmonic hot-carrier-mediated tunable photochemical reactions**
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Hot-carrier generation from surface plasmon decay has found many applications in many branches of physics, chemical, materials, and energy science. Especially, recent efforts indicated that the hot-carriers generated from plasmon decay in nanoparticles can transfer to attached molecules and drive the photochemistry of impossible in previous thought. In this work, we explored the atomic-scale mechanism of plasmonic hot-carrier mediated chemical reaction exampled by H\textsubscript{2} dissociation by employing time-dependent density functional calculations theory and non-adiabatic molecular dynamics. The numerical simulation demonstrates that the anti-bonding state of the attached molecule is found to be slightly higher than the Femi level and the potential energy surface of the excited state of the attached keeps the anti-bonding feature. Consequently, the hot-carriers generated from the nanoparticle can transfer to the anti-bonding state of the attached molecule and drive the photochemical reaction. Then, we also found chemical reaction is tunable if the molecule is placed in the center of the plasmonic dimer. The reaction rate can be either suppressed or enhanced depending on the geometry. In general, symmetry broken is essential to enhance the reaction rate. Thus, our work demonstrates the possibility of tunable photochemistry via plasmonic hot-carriers.

COLL 626

Challenging the polymer barricades around quantum dots: keeping copper ions away from the surface during click reactions

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Functionalization of nanocrystals is essential for their practical application, but synthesis on their surfaces is limited by incompatibilities with certain key reagents, as well as a poor understanding of how the organic passivation layer protects the nanocrystal. The copper-catalyzed azide–alkyne cycloaddition is among the most useful methods for ligating molecules to surfaces, but it has been largely useless for semiconductor quantum dots (QDs) because Cu ions quickly and irreversibly quench QD fluorescence. To discover nonquenching synthetic conditions for Cu-catalyzed click reactions on QD surfaces, we developed a combinatorial fluorescence assay to screen over 2000 reaction conditions to maximize cycloaddition efficiency while minimizing QD quenching. We identify conditions for complete coupling without significant quenching, which are compatible with common QD polymer surfaces and various azide/alkyne pairs. Based on insight from the combinatorial screen and mechanistic studies of Cu coordination.
and quenching, we find that both Cu\(^+\) and Cu\(^{2+}\) can quench quantum dot fluorescence, each with a different mechanism: Cu\(^+\) ions can pass through the organic barrier to quench QDs irreversibly, while Cu\(^{2+}\) ions are tightly coordinated to polymer surface carboxylates and can act as charge traps. Addition of excess QD ligands such as oleic acid reduces but does not eliminate Cu\(^+\) quenching, suggesting that even well-packed organic passivation layers are at least somewhat porous. Synthetically, full click coupling is possible with superstoichiometric concentrations of Cu accompanied by an excess of Cu\(^+\) ligands that selectively compete the Cu from the QD surface but allow it to remain catalytically active. Applied to the conjugation of am ion channel-specific peptidyl toxin to CdSe/ZnS QDs, we synthesize unquenched QD conjugates and image their specific and voltage-dependent affinity for ion channels in live cells.

**COLL 627**

**Energy transfer controlled by the semiconductor nanocrystal to ligand interface**

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Photon upconversion is a strategy for redistributing light energy, which takes one high energy photon and splits it into two lower energy photons, that can improve semiconductor-based devices from solar cells to photodetectors. One promising avenue towards achieving upconversion is to implement organic-based upconversion assisted by semiconductor nanocrystals. The mechanism of upconversion hinges on energy transfer across the nanocrystal surface to an organic molecule. Thus, understanding the nature of nanocrystalline surfaces and how these surfaces mediate the energy transfer process is crucial to implementing upconversion strategies in devices. The role that the ligand plays in transmitting energy as well as its impact on the surface chemistry of the nanocrystal is explored in several systems: PbS and Si nanocrystals paired with acene and perylenediimide molecules. Solution-based ligand exchange chemistry is found to induce the formation of surface-associated states which are long-lived and serve as an intermediate in the transfer process. This work offers insight into the interplay between nanocrystal surface functionalization and energy transfer efficiency.

**COLL 628**

**Understanding charge transfer from semiconductor nanocrystals to organics following LSPR excitation**

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Organic semiconductors are regarded as promising materials for the advancement of photovoltaic electronics. Generating current in these systems typically occurs through direct excitation of the molecule, requiring high-energy visible light. However, for applications such as solar cells, which look to utilize the entire solar spectrum, it would
be advantageous to provide an additional lower-energy route for charge generation. Plasmonic metal-oxide nanocrystals absorb high concentrations of light in the near-IR region of the electromagnetic spectrum, and have free electrons whose energies match the HOMO/LUMO levels of some prevalently studied organic semiconductor materials. By exciting the plasmon of a metal-oxide nanocrystal we can create hot electrons and hot holes that may transfer from the nanocrystal into a nearby organic molecule, creating excited states. These excited molecular states may be used for photovoltaics, as well as photocatalysis or even photon upconversion using triplet states. We look to understand the fundamental processes behind extracting these hot carriers at ITO and FICO nanocrystal/organic semiconductor interfaces using ultrafast transient absorption spectroscopy in order to better implement this photoinduced phenomenon.

**COLL 629**

**Investigating the energy transfer between organic and inorganic semiconductor two-dimensional material**

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Despite the low production cost and good mechanical properties of the organic solar cells (OSC), their power conversion efficiency is low compared with other solar cells. Enhancing the solar efficiency of the OSC is one of the exciting goals of the materials science research. Semiconducting two-dimensional materials (S2DM) is characterized by their ultrathin structure and high optoelectrical efficacy. Combining the polymer used in the OSC with the S2DM in a hybrid structure makes it possible to enhance the cell efficiency through energy and/or electron transfer. Studying the organic solar materials-S2DM interface area using ultrahigh resolution optical and microscopic techniques makes it possible to optimize the assembly of such materials inside the cell to improve their efficiency. The energy transfer between the conjugated polymer thin film such as P3HT and S2DM as MoS\textsubscript{2} were studied. The band gap of the MoS\textsubscript{2} is lowered as a result of electron and/or energy injection from the P3HT. The high-resolution optical measurements conducted for the MoS\textsubscript{2}-P3HT showed a great dependence on the thickness of an inert polymer spacer separated them. The photoluminescence (PL) measurements accorded well with the optical measurements. However, a red-shift in the PL peak was observed in case of the MoS\textsubscript{2}-P3HT in absence of the polymer spacer. The amount of shift is decreased by increasing the thickness of the polymer spacer. The characteristic Raman bands of the MoS\textsubscript{2} are shifted to a higher frequency as the thickness of the polymer spaces increased.

**COLL 630**
Characterizing the Brownian diffusion of nanocolloid and molecular solutions: Diffusion ordered NMR spectroscopy versus dynamic light scattering

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Hydrodynamic size is a characteristic dimension that reflects the Brownian motion of macromolecules and nanoparticles in a fluid phase. This property is crucial when investigating the utility of Au nanoparticles, AuNPs, luminescent quantum dots, QDs, and polymeric materials in biology. Dynamic light scattering (DLS) has been the method of choice for acquiring such information, but given the strong dependence of the Rayleigh scattered signal on size, the technique tends to become less effective for probing small objects (e.g., QDs and oligomers). Comparatively, diffusion ordered spectroscopy (DOSY) is a relatively new technique, relying on NMR, that addresses the most stringent limitations of DLS. We have applied DLS and DOSY NMR to characterize the oleylamine-coated AuNPs, core and core-shell QDs capped with either hydrophilic or hydrophobic ligands as well as oligomers. Our data show that the two approaches provide comparable data when larger size nanocolloids are probed. However, we find that DOSY is more suited for a broader range of materials and sizes down to sub-nanometer scale. We will discuss the benefits and limitations of each technique, with a focus on the effectiveness of DOSY for probing colloidal dispersions.

COLL 631

Point of anchor: Charge transfer between acetylenyl ligands and nanoparticles

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Photoinduced charge transfer across the metal oxide–organic ligand interface plays a key role in the diverse applications of metal oxide nanomaterials/nanostructures, such as photovoltaics, photocatalysis, and optoelectronics. Thus far, most studies are focused on molecular engineering of the organic chromophores, where the charge-transfer properties have been found to dictate the photo absorption efficiency and eventual device performance. Yet, as the chromophores are mostly bound onto the metal oxide surfaces by hydroxyl or carboxyl anchors, the impacts of the bonding interactions at the metal oxide–ligand interface on interfacial charge transfer have remained largely unexplored. Herein, acetylene derivatives are demonstrated as effective surface capping ligands for metal oxide nanoparticles, as exemplified with TiO₂, RuO₂, and ZnO. Experimental studies and first-principles calculations suggest the formation of M–O–C≡C– core–ligand linkages that lead to effective interfacial charge delocalization, in contrast to hopping/tunneling by the conventional M–O–CO– interfacial bonds in the carboxyl-capped counterparts. This leads to the generation of an
interfacial state within the oxide bandgap and much enhanced sensitization of the nanoparticle photoluminescence emissions as well as photocatalytic activity, as manifested in the comparative studies with TiO2 nanoparticles functionalized with ethynylpyrene and pyrenecarboxylic acid. These results highlight the significance of the unique interfacial bonding chemistry by acetylene anchoring group in facilitating efficient charge transfer through the oxide–ligand interfacial linkage and hence the fundamental implication in their practical applications.

Coll 632

Dendrimer-stabilized gold nanoflowers embedded with ultrasmall iron oxide nanoparticles for multimode tumor theranostics

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Development of multifunctional theranostic nanoplatforms for multimode imaging-guided combination therapy that can significantly improve the diagnostic sensitivity and therapeutic efficiency of tumors still remains a great challenge. Herein, we report a unique multifunctional theranostic nanoplatform based on generation 5 (G5) poly(amidoamine) dendrimer-stabilized gold nanoflowers embedded with ultrasmall iron oxide (USIO) nanoparticles (NPs) for multimode $T_1$-weighted magnetic resonance (MR)/computed tomography (CT)/photoacoustic (PA) imaging-guided combination photothermal therapy (PTT) and radiotherapy (RT) of tumors. In this study, we separately prepared G5 dendrimer-stabilized Au NPs and citric acid-stabilized USIO NPs, mixed the two particles under a certain Fe/Au molar ratio to form complexes, exposed the complexes to Au growth solution to form nanoflowers (NFs) via a seed-mediated manner, and acetylated the remaining dendrimer terminal amines. The formed dendrimer-stabilized Fe$_3$O$_4$/Au nanoflowers (for short, Fe$_3$O$_4$/Au DSNFs) have a mean diameter of 99.8 nm, display good colloidal stability and cytocompatibility, and exhibit a
near infrared absorption feature. The unique structure and composition of the Fe$_3$O$_4$/Au DSNFs endowed them with a high $r_1$ relaxivity (3.22 mM$^{-1}$s$^{-1}$) and photothermal conversion efficiency (82.7%), affording their uses as a theranostic nanoplatform for multimode MR/CT/PA imaging and combination PTT/RT of tumors with improved therapeutic efficacy, which is important for translational nanomedicine applications.

**COLL 633**

**Role of shape, chemical heterogeneity, and modulus on bacterial adhesion**

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The adhesion of bacteria from solution to a surface is the first step in biofilm formation, a high undesirable event in medical applications but a critical one in filtration and applications targeting removal of bacterial from solutions. Most studies of bacterial capture focus on surface chemistry, though recent research indicates other factors such as interfacial mechanics are important and can even dominate the fate of biomaterials. This talk explores specific factors affecting bacterial capture: (1) surface chemical heterogeneity, both on an engineered surface or on the bacteria themselves and (2) the specific influence of flow. The latter is addressed not simply in terms of the strength of the shear field but in terms of how the flow field couples with other features for instance on how heterogeneity couples flow particle rotations in flow to affect capture. Additionally we compare the capture of rod shape synthetic particles of different aspect ratios to those of bacteria to gain insight into E. coli capture. Regarding the influence of cell shape we additionally demonstrate the impact of the presence of flagella (compared with E. coli engineered without flagella), and we address cell aspect ratio through comparison between E. coli and silica rods. Here we show how cartwheel, log-roll, and stabilized torpedo trajectories influence cell adhesion. Finally, we present results on the impact of the surface modulus on bacterial capture and adsorbed configuration, the latter potentially influencing the subsequent colony growth.

**COLL 634**

**Biofilm bridge formation of Staphylococcus aureus biofilms, a gram positive bacteria, on slippery, lubricant-infused porous surface**

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A biofilm is an accumulation of microbial cells that adhere to a surface and form a complex microbial community with a polysaccharide matrix. Biofilms form at a solid-liquid interface and are commonly found in flowing water sources such as rivers and streams, as well as pipes and tubing. A common way of studying biofilms is by growing them on Slippery lubricant-infused porous surface (SLIPS). The hydrophobic pattern is coated with a biofilm repellent lubricant, krytox, while the hydrophilic is covered in water. Biofilms have previously been known to form bridges of bacteria over the repellent coated patterns, connecting biofilm clusters on multiple hydrophilic patterns. How these bridges are formed and what factors play into their formation, is still unknown. Previous research has been done on gram negative bacteria, such as Pseudomonas aeruginosa 30 and 49, and Stenotrophomonas maltophilia, which exhibit biofilm bridge formation. Based on this research, our research goal is to determine if Staphylococcus aureus, a gram positive bacteria, form biofilm bridges on the SLIPS. A series of growth experiments were conducted to view the formation of biofilm bridges of Staphylococcus aureus biofilms. Three growth patterns were observed during the experiment, growth with bridge formation, static growth that grew around the pattern surfaces and bacteria growth that crossed over the lubricant-infused hydrophobic patterns. This research will assist in challenge of preventing biofilm formation by learning how these biofilm bridges form and examining if this is an important factor in the spreading of biofilm.

**COLL 635**

**Novel microbe-resistant hybrid membranes for healing burns, wounds, and scars**

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There were about 550,000 burn injuries that received medical attention in the United States in 2017, of which majority were related to first- and second-degree burns. Burns are among the most painful and debilitating wounds and often turn deadly when infection sets in. Till date only a handful of FDA-approved products are available in the market to treat 2nd or 3rd degree burns and scars. Topical agents in treating wounds such as chlorhexidine, proflavine, iodine, H₂O₂, silver etc. have been used to combat wound infections. However, the relentless emergence of antibiotic resistant strains of pathogens, often with multiple antibiotic resistances, together with the discovery of novel antibiotics has led to the need to find alternative treatments.

Herein, we exhibit a novel and cost-effective microbe-resistant “hybrid” membranes engineered using hydrophobic modification, intercalation and exfoliation of organo-modified silicate-based materials and metal ions to prevent infections from ESKAPE pathogens without using expensive or environmentally toxic ions and nanoparticles viz. silver, copper etc. while promoting rapid wound and scar healing. Initial results from the physico-chemical and mechanical analyses have shown optimal moisture transport.
through the films - an important feature to accelerate the healing cascade for quick recovery. Antimicrobial efficacy tests using *B. subtilis* bacteria on Ag-clay films showed 100% effectiveness in 18h when compared to controls (silvadene ointment and no treatment). Antimicrobial tests included: (1) zone of inhibition evaluation based on Kirby-Bauer antimicrobial susceptibility test and (2) kill time study evaluation based on USP-51 antimicrobial effectiveness tests. This unique “hybrid” system promotes: (a) prevention and control of both gram-negative and gram-positive bacteria, (b) nontoxic and biodegradable features with optimal O$_2$ and moisture transport through the membrane, (c) easy application on wounds.

![Antimicrobial Tests](image)

Microbial efficacy test

**COLL 636**

**Single-cell optical trapping technique for real-time antibacterial characterization of novel wound management materials**

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Conventional methods of antibacterial characterization assume homogeneity in the effects of inhibitory agents on a bacterial population. Current research aims to uncover the heterogeneity of these effects by utilizing single-cell methods of characterization, but many of these methods utilize microfluidic-based devices which limit the types of agents that can be studied. Specifically, these devices are incapable of studying the inhibitory activity of agents such as polymeric matrices, which have been used extensively in the development of wet wound management materials. These wet wound management materials have been shown to proliferate skin cell growth and increase oxygen permeation, resulting in faster rates of healing. Furthermore, these materials are frequently modified with metal nanoparticles (MNPs) to enhance antibacterial properties and mitigate bacterial growth while preserving the biomimicry required for skin cell regeneration. While the mechanism of cell death due to colloidal MNPs has been extensively investigated, minimal attention has been given to the mechanisms of cell death attributed to MNP-functionalized polymeric substrates. To further uncover these mechanisms, this research utilizes epi-fluorescent optical tweezers to investigate their
antibacterial properties. Specifically, a single *E. coli* cell is optically trapped and non-covalently docked to a functionalized polymer matrix, after which cell lysis kinetics are monitored in real-time via fluorescent cell viability indicators. Inhibitory effects of Ag NP-incorporated matrices showed increased antibacterial activity related to the Ag\(^0\) concentration and size of the colloidal NPs. Additionally, non-covalent functionalization of Au NPs with select antibiotics has shown increased antibacterial activity when compared to trisodium citrate-capped Au NPs, demonstrating the tunability and effective delivery capabilities of the nanocomposite matrix.

**COLL 637**

*Multiphoton, FRET-based, theranostic nanoplatfor for two-photon bioimaging and two-photon excited photodynamic therapy of multiple drug-resistant bacteria*

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Near-infrared (NIR) light between 700 and 2500 nm has the capability to penetrate biological tissues and blood, which provides a huge advantages of higher penetration depth. However, because of the lack of available biocompatible single photon probes in NIR window, there is an urgent need for new theranostic material, which could be used for two-photon bioimaging as well as for two-photon photodynamic therapy (PDT) in biological window. Here we will discuss our recent reports on gold nanoclusters (GNCs) attached graphene quantum dot (GQD) based two-photon excited theranostic nanoplatfor with high two-photon absorption, very strong two-photon luminescence, as well as two-photon stability in NIR region. Experimental result shows strong two-photon luminescence and two-photon-induced PDT, which is based on fluorescence resonance energy transfer (FRET) mechanism, where graphene quantum dots with very high two-photon absorption act as two-photon donors and gold nanoclusters act as acceptors. Reported data indicate that \(^1\)O\(_2\) generation efficiency enhances tremendously due to the FRET process, which increases the two-photon excited PDT efficiency for multiple drug resistance bacteria (MDRB).

**COLL 638**

*Metal-protein nanocomposites with bactericidal and antibiofilm efficacies*

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Antimicrobial resistance (AMR) is causing 50 thousand deaths per year in Europe and North America, with a concomitant heavy economic burden. Bacteria have developed different specific antibiotic resistance mechanisms such as, altering or destroying the
antibiotic molecules, decreasing the membrane permeability to the antibiotic or expulsing it through efflux pumps. Besides these resistance mechanisms, the appearance of AMR is aggravated by the ability of bacteria to proliferate adhered to living tissues or inert indwelling devices forming biofilms. Bacteria encased in these structures avoid the immune system response and makes them highly tolerant to high concentrations of antimicrobials. Furthermore, conventional antibiotics do not remove biofilms thus, despite a successful antibiotic treatment; remaining sessile cells may lead to an infection relapse.

Metallic nanoparticles (MeNPs) are increasingly used to target pathogenic agents as an alternative to antibiotics. These nanoparticles present multiple biocidal mechanisms that occur at the same time (oxidative stress induction, metal ion release, or non-oxidative mechanism) requiring unlikely multiple simultaneous gene mutations for the appearance of the microbial resistance. Moreover, MeNPs can be conjugated with enzymes and peptides that present bactericidal properties to increase their effectiveness. On the other hand, among antibiofilm strategies, different enzymes can be applied to prevent the biofilm formation or its eradication once established.

In this study, we integrate MeNPs with either enzymes or bactericidal peptides to form a nanocomposite that combines synergistically different antimicrobial efficacies. The enzymatic component disrupts the bacterial communication pathways, through the hydrolysis of small molecule signals, that govern the biofilm formation. Meanwhile, the MeNPs and peptides provide multiple biocidal mechanisms to the nanocomposite. This antimicrobial approach could be applied in the form of coatings on surfaces such as hospital textiles, water treatment membranes and implantable medical devices, ensuring a safer environment for both patients and healthy population.

**NANO-FOREST CHITOSAN-GELATIN FILMS: AN IMPLANT COATING MODEL FOR ENHANCED BONE REGENERATION**

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Biomimicry strategies are being commonly used in the design of nano-biomaterials. Particularly, non-lithographic techniques (drop-casting, mold embossing etc.) have shown great potential in the facile fabrication of nanotextured platforms at large scale production. Orthopedic biomaterials or coatings possessing such nanoscale features
induce desirable interactions between bone tissue and implant surface, also known as osseointegration. In this study, nano-forest chitosan-gelatin (C:G) blend films were fabricated using nanoporous anodic alumina molds, and their antibacterial properties as well as osteogenesis potential was tested by comparing to the flat C:G films and tissue culture polystyrene (TCP) as controls. *In vitro analysis* of the expression of RUNX2, OPN and OCN genes for mesenchymal stem cells (MSCs) as well as osteoblast-like Saos 2 cells was found to be increased for the cells grown on nano C:G films indicating early stage osteogenic differentiation. Moreover, the mineralization tests (quantitative calcium analysis and alizarin red staining) showed that nano-topography significantly enhanced the mineralization capacity of both cell lines. This work may provide a new perspective of biomimetic surface topography fabrication for orthopedic implant coatings with superior osteogenic differentiation capacity and fast bone regeneration potential.

**COLL 640**

**Lectin-conjugated nanocarriers to treat chronic oral diseases**

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Drug nanocarriers capable of fast adhesion to cells is crucial in the localized delivery of drugs to treat chronic oral diseases. Presently it is clinically managed with topical formulations for immediate therapeutic effect. Studies have shown that lectins act as second generation bioadhesives showing ‘cytoadhesive’ properties by specifically recognizing sugars at the cell surface. We present studies with Wheat Germ Agglutinin (WGA) conjugated liposomes demonstrating a significant (*p*<0.05) increase in liposome binding with oral keratinocyte cells (OKF cells) compared to non-lectin liposomes within a short incubation time of 1 minute. This rapid binding allows the nanoparticles to attach onto oral cells before being flushed out by saliva, potentially reducing the need for frequent dosing. Fluorescence and cell viability studies with oral cells and *Streptococcus mutans* co-cultures demonstrated biocompatibility and that the sustained release of a model antibiotic by the attached liposomes is sufficient to show potent antimicrobial activity.

To treat the multiple clinical manifestations (example: infection, inflammation, pain) the co-administration of multiple classes of drugs is required. While liposomes are ideal nanocarriers for sustained drug release, it’s poor encapsulation and release control with hydrophobic drugs is a problem. Recent studies have utilized drug-cyclodextrin complexes to enhance the encapsulation of hydrophobic drugs into liposomes. We present the synthesis and characterization of novel cyclodextrin grafted WGA liposome nanocarriers for the dual encapsulation of both hydrophilic and hydrophobic drugs. These nanocarriers act as single vessel to hold many classes of drugs and show simultaneous sustained release to oral cells. Our studies suggest that the fast binding nature of lectins with oral cells can be exploited to develop novel sustained release nanoparticles for the localized treatment of chronic oral diseases.
COLL 641

Ag-Cu alloy nanoparticle synthesis and targeting infection in osteoblast cells

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Ag-Cu alloy nanoparticles (NPs) release Ag⁺ and Cu⁺ ions which are known to have strong antimicrobial activity, but the toxicity of metallic nanoparticles to host cells undermine their use in the therapeutic applications. This talk will discuss the strategy of forming the Ag-Cu metallic alloy nanoparticles at cold temperature conditions with functional groups on the nanoparticle surface for bio-conjugation to target intracellular infection. Internalized Staphylococcus aureus (S. aureus) bacteria in host cells have developed mechanisms to evade immune response by adopting the phenotype-small colony variant which can persist and survive for longer periods. As a result, the treatment of osteomyelitis due to S. aureus infection has become difficult. Antibiotic treatment against internalized infection may become inefficient due to low penetration of antibiotics, low retention in cells and a high probability of developing antibiotic resistance. Hence our NP treatment strategy which involves the on-site release of ions from the NPs can overcome intracellular infection. In this work, Ag-Cu alloy NPs are targeted to the osteoblast cell membrane via Integrin or Cadherin targeting antibodies. We observed that 4 to 6 hours after targeting, nanoparticles were internalized in the endosomes. The pH of early endosomes and lysosomes is slightly acidic which accelerates the process of ion release from the NPs. Ag⁺ and Cu⁺ ions released in the intracellular environment exhibited potent antimicrobial activity where more than 90% of the infection was cleared in 24 hours of incubation and the effectiveness of the particles was tested until 72 hours of incubation. In addition, this method of targeting bone infection minimizes the use of metallic nanoparticles to avoid toxicity to host cells, which may have clinical application for osteomyelitis management and needs to be studied in animal models.

COLL 642

Antibacterial polyurethane foam with incorporated lignin-capped silver nanoparticles for chronic wound treatment

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Incidences with chronic wounds among the elderly and patients with diabetes mellitus are increasing annually. Complications related with the chronic wounds include huge economical costs of the healthcare systems and heavy bacterial colonization which result in limb amputation, sepsis and ultimately death.

Antibacterial polyurethane foams have been prepared for treatment of cutaneous
infections by using different strategies, such as incorporation of quaternary ammonium, imidazolium or pyrrolidonium cationic groups and physiosorption of silver-based nanoparticles. However, the polyurethane foams with incorporated cationic groups can act on contact-killing principle, while the foams prepared by silver nanoparticles physiosorption are characterized by loss of antimicrobial properties due to their leaching over time. Therefore, polyurethane foams with covalently grafted nanoparticles for sustained release over the time of application are expected to possess superior properties over the physically linked counterparts.

In this work we synthesized polyurethane foams by dispersing lyophilized antibacterial Ag-lignin nanoparticles in the polyl-containing pre-foam solution. Lignin, which was used as a silver reducing and nanoparticle capping agent in this formulation, is underutilized waste material from many industries and was used as an additive to polyurethane formulations due to its high polyphenol content, reactive towards the isocyanates. The prepared polyurethane foams were shown to possess broad antibacterial activity against gram-positive and gram-negative bacterial strains. The foams revealed sustained release behaviour over time which is prerequisite for effective eradication of broad spectrum of bacterial strains in the bacteria-divergent chronic wound microflora.

**COLL 643**

**Microfluidic synthesis of hollow nanoparticles by using flow-induced interfacial self-assembly of polystyrene-block-poly(ethylene glycol)**

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Hollow nanoparticles (HNPs) have recently attracted an extensive attention due to a potential to be applied to the fields of nanoreactor, drug encapsulation and delivery. Differently from the conventional methods that require the multiple and complicated process of HNPs synthesis, this paper suggests a single step flow-induced microfluidic synthesis of HNPs by employing self-assembly of polystyrene-block-poly(ethylene glycol) (PS-b-PEG) in interface of a laminated flow formed in a double-focused microchannel. The formation process of the HNPs in laminar flow interface of the double-focused microchannel was illustrated in Figure 1. The polymer stream, pure solvent stream, and water stream were introduced into the inlet 1, 2 and 3, respectively. When the water meets with the polymer in the second focusing channel, the nucleation and dispersion processes occurred. Due to the transverse diffusion of the polymer stream and the water stream through the laminated flow interface, the self-assembly of PS-b-PEG occurred to form the HNPs. The polymerized HNPs moved to the outlet and were collected in a vial. Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) determine the hollow structure of the HNPs and their size. A narrow size distribution of the synthesized HNPs was
obtained compared with other microfluidic synthesis methods. The uniform size HNPs can be applied to drug encapsulation for pharmaceuticals and biomedical researches.

Figure 1. Schematic illustration of formation mechanism of the HNPs in the interface of the laminated flow formed in the double-focused microchannel: (0) Multi-laminated flow formed in the microchannel; (1) Dispersion and nucleation; (2) Growth through aggregation; (3) Self-assembly and TEM (a), (b) and SEM (c), (d) of the synthesized HNPs.

**COLL 644**

Sealable spherical mesoporous silica shell nanoreactors as fiducial nanoscale probes for x-rays

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Molecular reactions are often used as dosimetric probes. A major problem with using these aqueous reactions to determine the dose of ionizing radiation, however, is that other species, such as nanoparticles or other chemicals, either purposely or accidentally placed in solution often interfere with the reactions. The results measured in the presence of nanomaterials and scavengers therefore cannot be correctly interpreted based on the calibrated results free of the interfering species. Storing these molecular probes in nanoreactors can overcome this problem. Here we demonstrate for the first
time that it is possible to place typical probe molecules inside spherical hollow mesoporous silica shells and seal the pores after impregnation for the purpose using the so-formed nanoreactors as X-ray dose probes. The reactions are isolated from the external environment while the sealed shells still allow X-rays to freely penetrate through the walls of the nanoreactors. These nanoreactor probes can therefore fiducially report the dose of X-rays whether the nanoreactors are in solutions, in dry form, or in the presence of scavengers and catalysts in solution.

**COLL 645**

**Tuning the surface chemistry of graphene oxide nanoparticles for controlling drug release: modeling and experiments**

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Consolidation chemotherapy has been shown to increase overall survival and progression-free survival in patients affected by acute myeloid leukemia, lung cancer, and rectal cancer. Sustained single- or dual-drug release is crucial to minimize deleterious systemic side effects and maximize the desired response. In this context, nanomedicine has the potential to provide cost-effective and efficient solutions for releasing synergistic drugs with accurately controlled kinetics and molar dosage. Among the myriad of different nano-systems, graphene oxide (GO) particles show great potential as delivery systems in consolidation chemotherapy owing to their tunable surface physicochemical properties. Yet, tailoring the surface chemistry of GO nanoparticles to achieve precise synergistic ratio and controlled, sustained kinetics of drug release is a complex problem, with interplay between the drugs, and the type and degree of modification. To guide the surface chemical modification of GO particles to achieve controlled release of any desired combination of chemotherapeutics, we have developed a computational model based on atomistic molecular dynamic simulations that describe the adsorption and desorption of chemotherapeutic drugs irinotecan (IRI) and doxorubicin (DOX) onto GO particles modified with aliphatic primary/tertiary amines at different degrees of modification ($\chi$). The synergism of DOX and IRI has been demonstrated in multiple studies, showing that the efficacy of the IRI-DOX pair is enhanced when the molar release ratio is $> 1$. Our simulations accurately predict the adsorption of single drug molecules on virgin and modified GO surface, the formation of drug aggregates thereupon, and drug release by dissociation vs. detachment of the drug aggregates, at different values of solution pH (physiological 7.4 and tumor-like 5). Our experimental results fully validate the predicted release kinetics and ratio of both single- and dual-drug release from a wide variety of modified GO particles. Importantly, a modified GO formulation was identified that affords ideal release behavior (IRI/DOX ratio of 7.5 over 3 weeks).

**COLL 646**
Development of magnetic surfactants for low energy separations: Effect of surfactant stability on magnetic response

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The development of low energy, magnetically driven separations techniques offer a means to address the growing energy demands for chemical and biological separations. In order for magnetically-driven separations to be realized, additional research must be performed to determine fundamental structure-property relationships for magnetic surfactants. Unlike previous reports of magnetic colloids utilizing paramagnetic nanoparticles, this research focuses on amphiphiles with the paramagnetic moiety either as the counterion (Type 1) or chelated (Type 2) to the surfactant. We have synthesized ionic surfactants with magnetic counterions, surfactants with the magnetic moiety chelated in the surfactant unimer, and block copolymer amphiphiles with multiple magnetic moieties. Our research shows that the strength of association of the paramagnetic moiety with the amphiphilic components in an aqueous environment is dependent upon the type of complex that contains the ferromagnetic ion. Utilizing electrochemical methods, we quantitatively determined the stability of the association between cationic and anionic surfactants with a corresponding magnetic counterion in aqueous solution and examined the effect the stability of the association has on the magnetic response. Additionally, we examined the ability of the magnetic surfactants to alter the surface tension at the air-water interface in response to a magnetic field and found that the ability to alter interfacial properties is strongly dependent upon not only the strength of the association between the magnetic and surfactant moieties of the amphiphilic molecules but also the stability of the magnetic moiety.

COLL 647

Controlled assembly and reduction of graphene oxide networks for conductive composites

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Graphene has attracted enormous interest in the scientific community as the first 2D material with exceptional mechanical, electronic and thermal properties. Pristine graphene is notoriously difficult to process for macroscale applications, to overcome this many people use graphene oxide (GO) instead. GO is water soluble and easily functionalised and so can be simply processed into various systems. GO lacks the exceptional electronic properties of graphene due to structural disorder, therefore an
important area of research is on the reduction of GO, which partly restores the structure and properties of graphene. Various techniques have been developed to perform the reduction step. We report a simple approach for preparing conductive Polymer Latex-rGO composites by using a latex-assembly method. After a treatment in the oven at low T, we can reduce the GO in situ. We make use of the inherent GO properties to optimise the aqueous composite fabrication, which is scalable and adaptable, and then restore conductivity with a simple, low temperature, heating step; opening up pathways to tunable electronic composite materials on a large scale.

COLL 648

Microfluidic based chips for SERS ultrasensitive detection

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Microfluidic platforms allow generating a highly-ordered assembly of uniform gold nanoparticles inside their microchannels through the pervaporation of the solvent (Figure 1A). Furthermore, the microfluidic approach enables the fabrication of uniform assemblies of any dimension or morphology. Surface-enhanced Raman spectroscopy, SERS, is an advanced analytical technique that can be used for the ultrasensible detection of analytes since it offers orders of magnitude increases in Raman signals. It occurs at the surface of a plasmon surface mainly due to the presence of strong electromagnetic fields generated after the plasmon excitation. Moreover, this effect could be more intense in the case of hierarchical nanoparticles assemblies due to an antenna effect as demonstrated by recent simulations.

While the plasmonic substrates made by drop-casting show poor uniformity that limits their potential plasmonic applications, the microfluidic approach gives rise to platforms with highly uniform and intense SERS activity (being both key parameter to achieve quantitative analysis and low detection limits (LOD). Herein we will show the fabrication and characterization of plasmonic platforms fabricated using Au octahedral nanoparticles synthesized through a wet chemical method. Besides, the sensing capabilities of the platforms will be analyzed by investigating the SERS efficiency using different Raman active analytes. For instance, experiment performed with Crystal Violet showed a LOD of 100 zM, which is several orders of magnitude lower than those found in the literature. Additionally, by assembling a 3D silica supercrystal before the 3D plasmonic supercrystal we demonstrated its potential applicability as microfluidic liquid chromatography-chip with SERS-based sensing capabilities.
Figure 1: (A) Schematic illustration of the evaporated microfluidic system used for self-assembled Au nanoparticles with a SEM micrograph of the nanoparticles assembly. (B) Raman optical image and SERS spectra and mapping at 1270 cm\(^{-1}\) for acid blue 25 and 1618 cm\(^{-1}\) in the presence of a mixture of 10\(^{-7}\) M of each analyte.

**COLL 649**

Building random alloy surfaces from intermetallic seeds as a general route to strain-engineered electrocatalysts

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The need for sustainable energy platforms drives nanocatalyst design and synthesis. In the case of fuel cells, Pt-based catalysts are common but suffer from high cost and poor durability. Typical routes to overcome the high cost and unfavorable surface-adsorbate interactions are to incorporate earth-abundant metals, either through a core@shell architecture or alloy formation; this addition decreases expensive metal loadings and tunes the surface-adsorbate interaction in accordance with the Sabatier principle. Here, the versatility of seed-mediated co-reduction (SMCR) is demonstrated with the deposition of PtM (where M = Ni, Co, Cu, or Fe) random alloyed shells on PdCu B2 intermetallic seeds, integrating the concepts of a core@shell architecture and alloyed surfaces into one nanostructure. Control of shell thickness and Pt:M ratios is
demonstrated, providing a general route to strain-engineered alloyed surfaces. The performance of these nanocatalysts was evaluated for the oxygen reduction reaction (ORR) as a function of shell thickness and shell composition, where PtCu and PtNi shells showed the highest activity and outperformed PtCu and PtNi references. Significantly, this work demonstrates the versatility of SMCR as a facile way to control the many levers of catalyst design within one platform.

**COLL 650**

**Janus liposomes: Gel-assisted formation and functionalization**

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A highly-yield procedure for preparing microsized (giant) unilamellar Janus liposomes via gel-assisted lipid swelling are developed. Confocal fluorescence microscopy reveals in detail that these new lipid colloidal particles display broken symmetry and heterogeneous surface chemistry similar to other types of Janus particles. An optimized formation procedure is presented, which reproducibly yields large liposome populations dominated by a single-domain configuration. Functionalized Janus liposomes are obtained by introducing biotin-conjugated lipid or charged lipids. Specifically, the biotin-conjugated 1,2-dioleoyl-sn-glycerol-3-phosphoethanolamine preferentially partitions into the liquid disordered phase of the lipid matrix, rendering these Janus liposomes asymmetrical binding capacity toward avidin. This affinity binding drives irreversible and domain-specific cluster formation among Janus liposomes, whose structure and size are found to depend on the domain configuration of individual liposomes and incubation time. Furthermore, adding negative charged 1,2-dipalmitoyl-sn-glycero-3-phospho-(1’-rac-glycerol) and/or positive charged 1,2-dioleoyl-3-trimethylammonium-propane into lipid matrix lead the formation of mono-charged or di-charged Janus liposomes. Comparing to neutralized Janus liposomes, these charged Janus liposomes show preferential clustering behavior, and salt effects, concentration effects are observed in this system. The electrokinetic motion under DC in microfluidic channel further exhibits the differences of these modified Janus particles.

**COLL 651**

**Formation of 2D semiconductors with mesoporosity**

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Mesoporous CdSe materials are promising photo-catalysts for water splitting as well as photo-sensitizers toward CO2 conversion in the presence of co-catalysts. Here, CdSe materials with moderate mesoporosity (0.1–0.2 cm³/g) and surface area (30-60 m²/g) have been synthesized via chemical ion-exchange in aqueous solutions. Sheet-like CdSe(ethylenediamine)₀.₅ were successively introduced to create homogeneous or
heterogeneous mesopores (4-8 nm). Orthorhombic and hexagonal structures of CdSe are individually obtained after reacting with S²⁻ and Fe³⁺, confirmed by XRD and HRTEM. For S²⁻ treated CdSe(ethylenediamine)⁰.⁵, residual sulfides were found predominately at the edges of the CdSe sheets with controllable substitutions of anions (S/Se=0.1-0.3). For Fe³⁺ treated CdSe(ethylenediamine)⁰.⁵, the original orthorhombic structure was transformed into hexagonal one (wurtzite), instead, with loss of most organic components. Formation of ion-induced mesoporosity in 2D semiconductors demonstrates potential catalysts and substrates for energy conversion reactions.

(a) HRTEM images of CdSe(en)⁰.⁵ (b-d) identified with two facets ([104]/[020]) and corresponding FFT patterns.

COLL 652

Layer-dependent charge transfer kinetics in atomically thin MoS₂: PbS/CdS quantum dot hybrids

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Two-dimensional (2D) materials, like graphene and MoS₂, exhibit unique layer-dependent bandgap transition which offers a great opportunity to design hybrid heterostructures through bandgap engineering. As combining with zero-dimensional (0D) quantum dots (QDs), the hybrids can possess greatly improved photoresponsivity via efficient interfacial charge transfer. Here, the kinetics of photoinduced interfacial charge transfer between MoS₂ and PbS/CdS QDs has been revealed by time-resolved photoluminescence (PL) microscopy, showing that the charge transfer rate increases with added number of MoS₂ layers and as a result of increased driving force the between conduction band edge of MoS₂ and PbS/CdS QDs. The manipulation of bandgap energy can also be achieved by using different size of QDs, given an enhancement of charge transfer rate by increasing the driving force in small QDs. We have evaluated the results with theoretical model of the Marcus theory, which is in good agreement with our observations. Understanding the interfacial charge transfer kinetics between QDs and 2D materials is crucial and useful for improving photon-to-current conversion efficiency in optoelectronics.

COLL 653

Switchable surfactants for the preparation of monodisperse, sinter-resistant, supported nanoparticle catalysts

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Established methods of preparing supported nanoparticle catalysts do not provide sufficient control over nanoparticle morphology. Classical methods typically require organic surfactants to passivate the nanoparticle surface to limit undesired size changes. Stabilizing ligands bound to the nanoparticle surface compete with reagents for active sites and typically significantly hinder catalytic activity. Commonly used methods of ligand removal, such as calcination, have detrimental effects on the catalyst as exposure to high temperatures often results in significantly increased nanoparticle size and, thus, decreased total surface area for catalysis. Previously, we demonstrated a novel method for synthesizing highly active, monodisperse, supported nanoparticles using a switchable surfactant (SwiS) system. In this method nanoparticle size is finely controlled throughout synthesis and deposition. Here, we show with X-ray photoelectron spectroscopy (XPS) that supported nanoparticles prepared with SwiS are completely surface-clean after deposition, eliminating the need for any traditional activation steps such as calcination. Additionally, it is demonstrated that a low-temperature calcination at 230°C of surface-clean supported nanoparticles has detrimental effects on nanoparticle size, dispersion, and catalytic activity. Supported nanoparticles prepared with SwiS are up to 700% more active in the hydrogenation of 4-nitrophenol than their calcined counterparts. Further, calcination results in the formation of an induction time in 4-nitrophenol reduction, demonstrating that calcination causes surface structure rearrangements unfavorable for catalysis.
Time evolution of CsPbBr₃ nanocrystal synthesis: Cesium-bromine complexation dictates growth

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Hot injection synthesis has been established as the optimal method for the production of cesium lead halide perovskites (CsPbX₃, X=Cl, Br, I). However, our fundamental understanding of the perovskite growth mechanism is very limited. Owing to the ionic nature of CsPbX₃, the growing of nanocrystal occurs within just a few seconds, greatly hindering mechanistic studies. The challenge is further compounded by the fact that synthetic strategies for structural control established in other semiconductor nanomaterials do not work well for CsPbX₃. Thus a better understanding of the growth mechanism may enable strategies for more sophisticated morphological targets which would further expand the range of applications that can benefit from the exceptional optical quality of the material.

In this work, we demonstrate a method to slow down the growth of CsPbBr₃ nanocrystals by limiting the chemical accessibility of bromine during a hot injection synthesis. Using 1-bromohexane as the halide source extends the growth time scale from a few seconds to tens of minutes. This slow growth allows us to monitor ex situ the evolution of products in the early stages of CsPbBr₃ formation. Using a combination of powder X-ray diffraction and high-resolution transmission electron microscopy, we observe the initial formation of CsBr, followed by Cs₄PbBr₆, and eventually CsPbBr₃. As the chemical environment remains substantially identical to that of a conventional preparation, these results suggest that the complexation of Br to Cs is, surprisingly, the critical step that initiates CsPbBr₃ nanoparticle nucleation, with Cs₄PbBr₆ playing the role of intermediate. Furthermore, we use this fundamental insight to produce CsPbBr₃ nanosheets through the simple control of Cs concentration under the slowed kinetics, demonstrating a manner of morphological control inaccessible under fast reaction kinetics.
Coll 655

Upconversion luminescence enhancement using patterned reflective surfaces with applications in security printing

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Upconversion phosphors produce luminescence at wavelengths shorter than that of the excitation source. The intrinsically poor quantum efficiency of upconversion nanocrystals (UCNC), particularly at low excitation power densities, is the major limitation for many potential applications of these materials. Plasmonic enhancement is one of the primary strategies being pursued to improve the efficiency of upconversion. UC brightness can be significantly enhanced in the vicinity of noble metal nanostructures. The “plasmonic strategy”, however, has its own set of limitations.
Plasmonic enhancement is based on near-field interactions between the UC particles and the metal surface, and is, therefore, effective only for particles within approximately 100 nm of the metal surface. Previously, we shown that it is possible to design patterned metal surfaces which exploit the diffractive and reflective properties to enhance the efficiency of upconversion. The primary advantage of this strategy is that the enhancement resulting from these optical effects can be extended to sample volumes far outside the near-field range of the metal surface. Here, we present recent advances in using large-area (>10cm²) 2D cavity arrays to dramatically enhance the brightness of highly resolved images printed on the arrays with upconversion inks. (See Figure) The 2D array design was optimized for UC enhancement based on finite-difference time-domain (FDTD) calculations. We will explore the photophysical mechanisms responsible for the observed enhancement and consider the potential applications in covert security printing.

False color image indicating the relative brightness of an upconversion luminescence image of a QR code printing using inks activated with upconversion nanoparticles on (left) patterned gold cavity arrays.smooth gold and (right) smooth gold.

**COLL 656**

**Role of gold oxidation state in the synthesis of Au-CsPbX₃ heterostructure nanoparticles**
Comprehensive synthetic control in the fabrication of hybrid nanoparticles is essential for the development of high-efficient optoelectronic and photonic devices. Recent advances in the synthesis of hybrid architectures, particularly for Au-chalcogenide hybrid nanostructures, have enabled an excellent degree of control on the composition, shape, and interfacial coupling that provides modified optical and electronic properties. However, synthetic control in the fabrication of more recently developed hybrid metal-semiconductor nanostructures such as Au-CsPbX$_3$ is still poorly understood. Here, we demonstrate a synthetic strategy for the selective deposition of Au metal or cation exchange in all-inorganic CsPbX$_3$ nanocrystals with the addition of Au$^{1+}$ or Au$^{3+}$ salts. We have discovered that the pathway that predominates in this reaction is dependent on the oxidation state of the Au salt. For instance, AuX$_3$ reacts with CsPbX$_3$ nanocrystals to undergo cation exchange, producing divalent cesium gold(I) gold(III) halide nanocrystals (Cs$_2$AuAuX$_6$). In contrast, AuX leads to the deposition of nanoscale metallic gold on the nanocrystal surface through the reduction of the Au$^{+1}$ ion by the perovskite ligand shell. Preliminary results demonstrate that hybrid Au–CsPbBr$_3$ nanoparticles can be synthesized with PLQY up to 70%, in stark contrast with similar Cd-chalcogenide heterostructures. Our work suggests that hybrid metal-semiconductor nanoparticles based on Au-CsPbX$_3$ can provide an ideal platform for applications in photon up-conversion, photo catalysis, and solution-processed solar cells.

**COLL 657**

**Light-assisted cation exchange in CsPbX$_3$ nanocrystals**

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CsPbX$_3$ perovskite nanocrystals has shown tunable bandgap through post-synthetic anion exchange. The B-site Pb$^{2+}$ cation, however, was believed to possess much lower mobility compared with that of halide anions. Therefore, most reported B-site cation doping used direct synthesis at high temperature such as hot-injection random doping rather than cation exchange. Fewer works showed that post-synthetic cation exchange is possible but extremely slow. In this work, we will show that the B-site cation have a great tendency to be replaced with the assistance of light induced anion exchange. CsPbX$_3$ nanocrystals were dispersed in saturated Mn$^{2+}$ haloalkanes solutions and treated with light above the bandgap of nanocrystals. Photoinduced reduction of solvent will release halide anion locally and following trigger anion exchange. This process drives the cations into the lattice of the surface of nanocrystal and further diffuse into the inside. This post-synthetic method could be universally applied to dope different cations including Mn$^{2+}$ and Yb$^{3+}$ into different systems including CsPbCl$_3$ and CsPbBr$_3$ nanocrystals. Moreover, anisotropic structures such as nanowires and nanoplatelets
could also be doped easily with this method. This work implies the potential of replacing Pb\(^{2+}\), which is toxic and hinders wide applications of lead halide perovskite materials, with non-toxic cations. The ability to use light to control the doping concentration as well as the chemical composition shows a great and unique potential of patterning the chemical transformation of CsPbX\(_3\) nanocrystals.

**COLL 658**

Deposition of graphene stabilized droplets for conductive surfaces

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Fabricating flexible electronics using electrically conductive ink has been investigated using electrically conductive inks that include metals, conductive polymers, and carbon materials. Metal-based ink often requires high sintering temperatures, conductive polymers suffer from long-term stability, and carbon materials normally require forming a stable suspension with additives that can degrade the performance of the ink. Here we present a one-step preparation of graphene ink with no post-high-temperature heating, stabilizers, or stability concerns. Our interfacial trapping method takes advantage of the fact that graphite does not form a stable suspension in either water or organic solvent. Instead, graphite resides at the interface in an oil/water mixture where it spontaneously exfoliates into graphene to lower the total energy of the system and is trapped in the interface. When the system is stirred or shaken, a water-in-oil emulsion with graphene stabilizing the interface is formed. When the oil phase is a long chain alkane, the viscosity of the emulsion is suitable for screen printing. The effect of using different alkane as the oil phase, and different graphite loading on the viscosity of the ink, electrical conductivity, resolution, and flexibility of the ink line are presented.

**COLL 659**

Directing nanoscale self-assembly through valence control

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The challenges of creating designed materials via self-assembly of nanoscale blocks require establishing robust yet highly tailorable methods for directing nanoscale interactions. While it has been recognized that anisotropic bonds might allow to control an interparticle coordination and to promote a formation of desired large-scale organizations, — the development of practical realizations was notoriously difficult. We have developed an assembly platform that through a regulation of nano-object valence permit controlling a symmetry of self-assembled structures. That approach offers an
assembly of prescribed nanoscale architectures and complex lattices. Moreover, a variety of nano-object types can be integrated into these self-assembled hetero-architectures. The applications of this assembly strategy for generating targeted nanoscale functional materials will be also discussed.

**COLL 660**

**Synthetic approaches for preparation of binary, heterogeneous nanoparticle composites for solid-state photonics**

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The pursuit of functional composites that impact a wide range of technologies, including optical or quantum information processing has stimulated significant interest in the preparation of hybrid material combining different inorganic nanoparticles (NPs) with polymers. Advances in NP-polymer composites requires nanostructured polymers and synthetic strategies that allow for spatially regulated arrangement, and ideally precision geometric positioning of the NPs in order to control their collective properties. Although a wide variety of polymers have been evaluated as stabilizing matrices for embedding NPs considerably few efforts have tackled co-integration of disparate NPs, such as combining hydrophobic (organosoluble NPs) with hydrophilic NPs (water soluble NPs). To address this opportunity, our efforts on the use of nanostructured polymerized ionic liquids (poly(IL)s) as scaffolding for the spatial organization or reactive matrix for in-situ synthesis of NPs will be detailed.

**COLL 661**

**Properties of three-dimensional flow-through electrodes made from solution-synthesized metal nanowires**

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Achieving a high rate of electrochemical conversion at a high efficiency in an electrochemical reactor requires the use of flow-through porous electrodes with a high surface area per unit volume, a high conductivity, and large mass-transfer rates. Several types of porous electrodes are commercially available, including carbon paper, graphite felt, reticulated vitreous carbon (RVC), metal mesh, and metal foam. However, these electrodes were all developed in the 1970’s, and there has been little innovation in this field for ~40 years. This presentation will describe the synthesis, fabrication, and properties of flow-through electrodes made from Cu nanowires. Cu Nanowires were synthesized in a basic solution by reducing Cu(NO₃)₂ by glucose in the presence of ethylenediamine. Filtration and annealing of Cu nanowires resulted in an electrode
porosity of 94%. Compared to carbon paper, which has the highest surface area of any commercially available flow-through electrode, the Cu nanowire electrode had 15 times more surface area and was 32 times more conductive. A disadvantage of the Cu nanowire electrode was its hydraulic permeability was 10 times lower than carbon paper. The Cu nanowire electrode could reduce Cu ions at a single-pass conversion of 70% at a flow rate 611 times greater than for carbon paper under mass-transport limited conditions (i.e. low concentrations of Cu ions). Under kinetically limited conditions (i.e. high concentrations of Cu ions) the Cu nanowire electrode could achieve a flow rate 10 times greater than carbon paper at a single pass conversion of 70%. The Cu nanowire electrode was also compared to carbon paper for the intramolecular cyclization of 2,2'-bis(bromomethyl)-1,1'-biphenyl to produce 9,10-dihydrophenanthrene via electrochemical reductive dehalogenation. The maximum productivity of the Cu nanowire electrode was 4 times higher than that of carbon paper, demonstrating the ability of Cu nanowire electrodes to improve the productivity of organic electrosynthesis.

**COLL 662**

**Synthesis and characterization of stimuli responsive poly(N-vinylcaprolactum-co-itaconic acid) microgel containing silver nanoparticles with tunable optical and catalytic properties**

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In this work, poly (vinylcaprolactum-co-itaconic acid) microgel was prepared by free radical polymerization. Silver nanoparticles were prepared in synthesized microgel networks by in situ reduction of Ag⁺ ions which were loaded in microgel from aqueous solution of AgNO₃. The prepared microgel was characterized by Fourier Transformation Infra Red Spectroscopy, UV-Visible spectroscopy, Fluorescence Spectroscopy, X-Ray Diffraction, Laser Light Scattering, Thermal Gravimetric Analysis, Differential Scanning Calorimetry and Transmission Electron Microscopy. Swelling behavior of microgel was studied as a function of temperature and pH. The microgel was found to be in swollen state at low temperature and basic medium while in collapsed state at high temperature and acidic medium. A slight decrease in swelling capacity of microgel was observed after the fabrication of silver nanoparticles. A red shift was observed in surface plasmon resonance wavelength of silver nanoparticles with pH induced swelling of microgel. Catalytic activity of the composite microgel was studied by using them as catalyst for the reduction of 4-nitrophenol. Effects of temperature and catalyst dose were also investigated. Activation energy for the catalytic reduction of 4-nitrophenol was found to be 28.4kJ/mol. The change in catalytic performance and shift in absorption maxima of composite microgel as a function of temperature and pH reveals that this system has potential to be used as tunable catalyst and optical sensor.

**COLL 663**
Molecular spacing of nanostructured carbon materials for energy storage: Synthesis and characterization

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The ability to store energy for later use is critical to the development of green energy sources. Batteries (specifically Li ion cells) are the dominant technology for electrical energy storage, with a large capacity, but low charge and discharge rates and much shorter effective lifetimes in comparison to supercapacitor technology. Supercapacitors, though, do not hold as much charge. Capacity can be increased in supercapacitors utilizing carbon nanotubes (CNTs) as electrode material in an electric double layer system through the CNTs' significant specific surface area, but aggregation of the CNTs reduces the ion accessible surface area. Our research has designed molecular spacers to bind to and intercalate between the CNTs to prevent aggregation while providing an electrically conductive network between the CNTs. Synthesis and characterization of a ligand featuring two ferrocenyl moieties and a phenol ring (38% yield) from which two complexes have been produced will be presented; the synthesis and characterization of a novel molecule which adds two additional phenol groups for increased binding will also be presented; and electrochemical characterization of thin films of these compounds intercalated as molecular spacers into nanostructured carbon materials will also be presented, including: cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy data. The presentation will show the effect of the molecular spacer on the specific capacitance, energy and power of these thin film electrical energy storage devices.
Nanostructured graphite-based materials for hydrogen energy storage

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In 1999, Orimo\(^1\) reported that nanostructured graphite produced by milling could absorb up to 7.4 wt% hydrogen. However, high temperatures (up to 600 K) were then required to release this hydrogen, and it was not reversible. In 2005, Ichikawa et al\(^2\) reported that the addition of LiH introduces a degree of reversibility (i.e. allows some hydrogen re-absorption). Ball-milled graphite with Fe (1 at%) (10 bar H\(_2\), 80 h) was found to store more hydrogen than pure graphite milled under the same conditions\(^3\). However, for both these additions, methane was also released during desorption, which will prevent long-term reversibility. In our work, the effect of milling conditions and additions on the microstructure and hydrogen storage properties of graphite milled in a tungsten carbide pot was investigated using TGA, mass spectrometry, XRD, SEM, TEM, Sieverts-PCT and Raman spectroscopy. The TGA and MS results showed that, for a graphite sample milled in hydrogen for 10 hours, the amount of hydrogen desorbed was about 5.6 wt%, and the onset desorption temperature was about 400°C. No methane release could be detected up to 12 hours milling time. The physical properties have been characterised by HRTEM and Raman spectroscopy as a function of milling conditions. HRTEM showed that the interlayer distance changed with milling (Fig. 1). This work discusses how the milling conditions and the type of additions, effect both the structure of the graphite samples and their hydrogen storage properties.

Atomistic simulations of carbon nanotube deposition on functionalized silicon substrates

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Single-walled carbon nanotubes (SWCNTs) have wide applications in semiconducting devices due to exceptional electronic properties. Polyfluorene polymer PFO-BPy has shown to enable a high-fidelity sorting process that separates the desirable semiconducting SWCNTs from synthesized mixtures of metallic and semiconducting SWCNTs. Randomly distributed SWCNT thin film demonstrates suboptimal electronic properties, yet it is still challenging to organize SWCNTs into ordered structures. Therefore, it is essential to understanding the interactions between PFO-BPy wrapped
SWCNTs and substrates. In our complementary experiments, the deposition of SWCNT depends on the substrate chemistry, i.e. the type of self-assembled monolayer (SAM) of organic molecules that is grafted on silicon substrate. However, no linear correlation has been found between the hydrophobicity/hydrophilicity of SAMs and the deposition density and pattern. In order to provide mechanistic insights into this deposition phenomenon, we apply molecular dynamics (MD) simulations to study the adsorption of PFO-BPy wrapped SWCNT on different SAMs-grafted silicon surfaces. Four model SAMs (PFOTS, OTS, HMDS, and APTES) have been chosen to represent a wide range of hydrophilicity and hydrophobicity, i.e. different water-air contact angles.

**COLL 666**

**3-Dimensional templates from self-assembled 2-dimensional graphene**

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Placing graphite at a high-energy oil/water interface results in the spontaneous, thermodynamically driven exfoliation as the graphene sheets spread at the interface. This spreading lowers the free energy of the system as the two-dimensional graphene sheets act as surfactants. As such, the graphene sheets stabilize emulsions, and by polymerizing the continuous oil phase or monomers in the dispersed aqueous phase, electrically conductive porous composites or graphene coated spheres are synthesized. This approach uses natural flake graphite, not graphite oxide or reduced graphene oxide, and is thus inexpensive and scalable. The mechanism of exfoliation and applications such as synthesizing porous electrodes and hollow graphene spheres will be discussed. Shown in the image is a computational representation of graphene stabilized water droplets in a continuous oil phase.
Phosphorene is a promising semiconducting nanomaterial for electronic and optoelectronic applications. It exhibits tunable photoluminescence in the infrared, based on the number of phosphorene layers. However, phosphorene rapidly degrades in the presence of water and oxygen, which significantly limits its viability for real-world applications. In this work, we have developed a biomimetic strategy for encapsulation of pyrene-assisted exfoliated phosphorene for degradation stabilization. To control oxygen diffusion, which results in degradation, phosphorene has been encapsulated in self-assembled natural and synthetic lipid bilayers. The kinetics of degradation have been examined by measuring changes in lipid bilayer vesicle size using dynamic light scattering, fluorescence, and scanning probe microscopy. Additionally, the tunability of this biomimetic protective layer has been examined using vesicles composed of different lipid compositions and photo-crosslinkable lipids.
Vapor phase plotting of organosilane-based self-assembled monolayer (SAM) gradients is demonstrated for the first time. Patterned SAMs are formed by delivering gas phase organotrichlorosilane precursors to a reactive silica surface using a heated glass capillary. The capillary is attached via a short flexible tube to a reservoir containing the precursor dissolved in toluene. The proximal end of the capillary is positioned at an experimentally-optimized distance of 30 µm above the substrate during film deposition. The capillary is mounted to a stepper-motor-driven X,Y plotter for raster scanning above the surface. Two different organotrichlorosilane precursors are employed in this initial demonstration: n-octyltrichlorosilane and 3-cyanopropyltrichlorosilane. The dependence of SAM deposition on ambient relative humidity, capillary-substrate separation, raster scanning speed, and solvent viscosity and volatility are all explored and optimum deposition conditions are identified. The optimized procedures are used to plot uniformly modified square “pads” and gradients of the silanes. Film formation is verified and the gradient profiles are obtained by sessile drop water contact angle measurements, spectroscopic ellipsometry measurements of film thickness, and by X-ray photoelectron spectroscopy (XPS) mapping. The resolution of the plotting process is currently in the millimeter range and depends on capillary diameter and distance from the substrate surface. Vapor phase plotting affords an unique direct-write method for producing patterned and chemically graded SAMS that may find applications in microfluidic devices, planar chromatography, and in optical and electronic devices.

Optimized surface functionalization with self-assembled monolayers for enhanced alpha detection from uranium hexafluoride (UF₆)

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Passivated Implanted Planar Silicon (PIPS) detectors are commonly used for alpha particle detection. The efficiency of alpha particle detection from uranium hexafluoride, which has a low specific activity, might be improved by altering the detector to increase the UF₆ surface residence time. To this end, we have investigated coating the detector with gold and absorbing variously-functionalized alkylthiols to form self-assembled monolayers (SAMs) on the surface. We discuss optimization of the metal coating thickness to minimize energy spreading in the alpha spectrum, while maintaining SAM
quality. Monte Carlo simulations (using the AASI program) of the alpha spectrum are combined with surface analysis techniques (reflection-absorption infrared spectroscopy (RAIRS), x-ray photoelectron spectroscopy (XPS), and contact angle goniometry) to arrive at an optimized architecture. Chemical compatibility testing of sample structures is executed, in collaboration with Argonne National Lab, in a custom chamber that allows exposure to radiological species. The chamber has the ability for QCM (quartz crystal microbalance) and RAIRS studies of the surface, and is equipped with a mass spectrometer for monitoring gas-phase products. It can operate in pressures between ultra-high vacuum (UHV) and up to ~100 Torr of UF₆. We will report our progress and results of these chemical compatibility studies of the SAM surface toward UF₆ attack.

COLL 670

Enantiospecific interactions between chiral molecules and magnetic surfaces

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The Chiral-Induced Spin Selectivity (CISS) effect was reported for the first time in 1999, and later it was found that photo-electrons moving through a self-assembled monolayer of DNA showed a 60% spin-polarization. This effect shows that when electrons move through chiral molecules, their transport is spin-dependent, with the preferred spin-orientation determined by the handedness of the molecule and the direction of motion. More recent studies demonstrated that upon adsorption of a chiral self-assembled monolayer (SAM), a soft ferromagnetic layer could be permanently magnetized in one direction, depending on the handedness of the adsorbed molecule. This effect originates from the well-known phenomenon in which the formation of a SAM with a large dipole moment involves charge transfer that equalizes the electrochemical potential of the adsorbed layer and the sample surface: as a result of the CISS effect, this charge transfer is spin-polarized and thus can magnetize the ferromagnetic layer. Based on these studies, we investigated the complimentary phenomenon, the possible use of a magnetized ferromagnetic layer to induce enantioselective adsorption of chiral molecules.

The results indicate that the interaction of chiral molecules with a perpendicularly magnetized substrate is enantiospecific. Thus, one enantiomer adsorbs preferentially when the magnetic dipole is pointing up, whereas the other adsorbs faster for the opposite alignment of the magnetization. The interaction is not controlled by the magnetic field per se, but rather by the electron spin orientations, and opens prospects for a distinct approach to enantiomeric separations. These results suggest that the same approach can be used to achieve chiral resolution in the crystallization processes of conglomerates. The spin-polarized surface promotes crystallization of enantiomorphous crystals depending on the direction of the magnetic moment.
Chemically-functionalized N-heterocyclic carbene molecules (NHCs) provide unique molecular platform for the formation of chemically tunable self-assembled monolayers (SAMs). In this work, we have identified the stability, geometry and reactivity of NO$_2$-functionalized NHCs that were anchored on Au (111) surface by conducting X-ray photoelectron spectroscopy and polarizable near edge X-ray absorption fine structure spectroscopy measurements. The formation of strongly bound SAM with preferable horizontal orientation of the NHCs with respect to the Au surface was detected. Mild annealing (up to 200 °C) or exposure to X-ray radiation led to partial nitro reduction. Complete nitro-to-amine reduction was identified once the sample was annealed to 400 °C. The chemical changes were coupled with reorientation of the NHCs, which were flat-laying on the surface following high temperature annealing. These results demonstrate the dynamic nature of NO$_2$-functionalized NHCs-based SAM and the influence of reaction conditions on the chemical and structural properties of NHCs.
Patterned alkylsilane self-assembled monolayers for *in vitro* study of cardiac and neurodegenerative diseases

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The application of silane chemistry to silicon-containing substrates enables self-assembled monolayers with a wide variety of functional groups for use in controlling the adhesion and behavior of cultured biological tissues. In addition to directly controlling functional groups present on the surface, these self-assembled monolayers also influence the adsorption and activity of proteins that interact with adhering cells. Of particular interest are alkylsilanes containing polyethylene-glycol functional groups for cytophobic (cell repulsive) and aminosilanes containing diethylene triamine (DETA) functional groups for cytophilic (cell adhesive) surface chemistries. Using an excimer laser, these silane self-assembled monolayers were patterned to produce specific chemical patterns of cytophilic and cytophobic regions on microelectrode arrays. A uniform width pattern was created and aligned on the electrodes to control human induced pluripotent stem cell (iPSC)-derived cardiomyocytes to produce an in vivo-like alignment of the cardiomyocytes, and was used to measure electrical behavior including conduction velocity and field potential duration for use in studying cardiac disease. A separate pattern was created to form human iPSC-derived neurons into isolated groups of cell bodies while enabling communication between groups through cell processes. These interconnected groups of neurons were designed for use in studying neurodegenerative diseases. X-ray photoelectron spectroscopy (XPS) was used to characterize the silane self-assembled monolayers in terms of degree of deposition and removal via laser patterning. XPS was additionally used to quantify the amount of protein adsorbed onto the surfaces. Specifically, the carbonyl (C=O) peak was used as a protein-specific chemical moiety for determination of protein deposition on DETA-containing surfaces. This application of silane chemistries patterned through excimer-laser photolithography is a powerful tool for controlling cell behavior and enables the creation and study of cell-based structures on microelectrode arrays for measurement of electrical properties of these tissues.

 Modification of inorganic oxides with poly(hydridomethyl)siloxanes as an approach to mixed functional surfaces

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Over the last several years, reactions between siloxane polymers or monomers with inorganic oxide surfaces have become more prominent, owing to the increasing acceptance of the siloxane bond as a functional, reactive group. However, while these reagents create excellent low hysteresis surfaces, they do not provide for further functionalization. Poly(hydridomethylsiloxane)s (PHMS), on the other hand, react readily with a wide variety of inorganic oxide surfaces while providing a scaffold for subsequent functionalization. Herein, we discuss the preparation of PHMS-modified silica surfaces. Reaction conditions show a significant influence on the resulting surface, with temperature dependence on the dominant reaction mechanism. These PHMS surfaces also exhibit low contact angle hysteresis, but can also be further modified through cross-coupling reactions, such as hydrosilylation, to create more advanced monolayers. Surfaces are examined via dynamic contact angles, ellipsometry, and x-ray photoelectron spectroscopy (XPS) to show changes in the surface chemistry with subsequent modifications, and their effects on wettability.

COLL 674

Visualizing mineral-solution interfaces using 3D atomic force microscopy

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Understanding processes at solid-liquid interfaces is a key challenge for multiple research fields ranging from surface chemistry and heterogeneous catalysis to biomembranes and living cells. In mineral systems, interfacial hydration structure creates ion distributions, chemical potential gradients, and inter-particles forces that influence impurity adsorption, mineral nucleation, and growth by particle assembly. Recent advances in atomic force microscopy—specifically 3D fast force mapping in amplitude modulated mode—have allowed the direct observation of interfacial solution structure with sub-nanometer resolution. We use this capability to probe multiple mineral-solution systems, including layered silicates (phlogopite and muscovite mica) and aluminum (oxy)hydroxides (boehmite and gibbsite) exposed to salt solutions of different pH and ionic strength. Depending on the system, our data show three to five structured layers spaced 0.2–0.5 nm apart and extending ~1.5 nm from the surface, with lateral features templated by the underlying crystal lattice. We compare the results to molecular dynamics simulations and discuss the promises and limitations of this exciting technique.
Robust and transparent zwitterionic polymer with antifogging and self-cleaning properties under UV irradiation

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In this work, we have investigated a series of zwitterionic copolymers that demonstrate outstanding antifogging and self-cleaning properties. These polymer coatings are photochemically grafted to substrates containing C-H bonds with rapid kinetics and form a robust polymer networks on plastic and alkyl-modified glass surfaces. The copolymers consist of a zwitterionic monomer, which provides high hydrophilicity, and a benzophenone moiety that produces a densely cross-linked network. The optical clarity of the substrates is not impacted by the polymer coating, and even slightly improved due to the refractive index of the polymer. The antifogging and self-cleaning capabilities were determined by a series of experiments, where the optical transmittance of substrates modified with copolymer coatings was excellent under both hot and cold fogging conditions. Additionally, surfaces contaminated with oil are easily cleaned by simply submerging the coatings in water. Moreover, the coatings exhibit excellent chemical and mechanical resistance, and maintain antifogging properties after abrasion testing in the presence of either chemical detergents or common household cleaners.
Petroleum is still the main source of energy around the world, according to the International Energy Agency (iea.org). For its great significance, much effort is applied on more effective ways to extract the oil and isolate it, decreasing the number of steps and even reducing the time required for it. Among the hindrances, the formation of foam is a concern because of the reduced oil production capacity observed, result of the large overheads in the gravitational separators where water, oil and gas are separated. Among the methods for foam control, the more efficient is the application of antifoamers or defoamers, chemicals with properties to avoid foam to form or to break it in a short
time. The standard product used in this case is silicone oil, specifically polydimethylsiloxane (PDMS). Although it is very efficient as an antifoam agent, the silicon present in PDMS structure is converted to silicon oxide in the petroleum refining step, causing the poisoning of the hydro-treatment catalyst and the yield reduction. Much research has been done to reduce the amount of silicon in the antifoamers, but none with satisfactory results. Therefore, another approach has been made to understand what properties of PDMS make it so effective an antifoamer, and with those, been able to design a silicon-free polymer or a low-quantity silicon polymer with such characteristics.

At first, 5 PDMS commercial samples with distinct viscosities (5, 10, 20, 100 and 60000 cSt) were characterized by H-NMR and FTIR-ATR, and viscometric molar mass was determined. Formulations of these samples were prepared and the interfacial tension and the antifoam efficiency (method found in “J. Pet. Sci. Eng. 2011, 76, 172”) were tested. Physical-chemical properties, such as entrance, spreading and bridge coefficients, dielectric constant and permeability of gas were also investigated. In order to determine the formulation with the most effective performance, different solvents were also studied.

So far, it can be inferred that the higher the molar mass, the more efficient is the antifoam effect. However, viscosity should be adjusted so the agent may be properly solubilized. For that, the solvent has a major role, as it may synergize with the agent so to improve its access to the oil, allowing a faster time of action avoiding the formation of the foam.

**COLL 677**

**Surface reactivity of sodium silicate glasses in aqueous environment and its effects on mechanochemical wear: a ReaxFF molecular dynamics study**

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The chemical reactivity of glass surfaces affects many properties, thereby requiring thorough understanding of surface structure-property relationships before they could be processed and utilized as promising materials of industrial interest. Specifically, the presence of adsorbed water molecules and their interaction with leachable alkali ions at the surface is of particular concern, since the structural modifications that take place under different environment makes the characterization of glass surface complicated. While various experimental methods were designed to probe surface phenomena, computational methods have successfully provided key molecular details responsible for distinctive surface chemistry of glasses. In this work, we performed molecular dynamics (MD) simulations with the ReaxFF reactive force field to investigate glass-water interactions and their effects on the mechanochemical wear of glass surface. A sodium silicate, which is an archetype of complex multicomponent silicate glasses, was used to model the glass-water interface and the simulation results were analyzed focusing on the chemical modifications that occur at the surface. Within this glass-water reaction simulation, the initial stages of the glass dissolution and sodium leaching...
mechanisms were elucidated. To further address the role of water molecules and sodium ions, we carried out mechanochemical wear simulation of sodium silicate glass under a sliding contact with silica counter-surface using the same reactive MD framework. The results with pristine surface and sodium-leached surface as substrates indicate that surface conditions govern the kind of hydrous species formulated and the location of sodium ions under mechanical stress during the sliding. Overall, the atomic scale simulations in this work can provide physical insights to the mechanochemical wear resistance behavior observed in the experiments.

COLL 678

Pre-treatment of dentin with chondroitin sulfate modulates dentinal tubule occlusion by toothpaste components

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Tooth sensitivity and hypersensitivity is essentially pain due to stimulation of intradental nerves. Exposure of the dentin layer and patency of its corresponding tubules is agreed to be the main contributor of this stimulation. Common methodologies go about subsequent desensitization in two general ways: nerve depolarization or tubular occlusion. Both seek to mitigate the same problem: the pain generated by various extreme stimuli—thermal or hot/cold stimuli, being the most common.

This research was aimed at the activation of inactive ingredients of a dentifrice by the pre-treatment of the dentin substrate with a polysaccharide, aqueous (aq.) solution of chondroitin sulfate (ChS), which is found naturally in the dentin matrix, and L-arginine, a naturally occurring amino-acid.

Herein, we report a study that examines in an in vitro environment the potential of ChS and L-arginine to aid in the effectiveness of adhesion of toothpaste components to the tooth surface. The evaluation of two over-the-counter dentifrices Colgate® Cavity Protection and Sensodyne® Pronamel®, a toothpaste marketed specifically for addressing pain related to tooth sensitivity, is conducted in conjunction with the proposed pretreatment formulation. We found that: (i) Pre-treatment of dentin samples by an aq. solution of ChS significantly increased adhesion of the TiO$_2$ excipient from commercial toothpastes such as Sensodyne®. (ii) The deposit of a toothpaste excipient on dentin was resistant to washing with water and ultrasonication challenge. (iii) Pre-treatment of dentin samples by an aq. solution of ChS did not result in adhesion of non-TiO$_2$ containing commercial toothpastes such as Colgate® However, when Colgate® was mixed with 5wt% hydroxyapatite or calcium carbonate, the adhesion of particles to tooth surface and occlusion of dentinal tubules was significantly increased. (iv) Pre-treatment of dentin with L-arginine does improve adhesion of calcium carbonate particles, but not as efficiently as ChS. The collected data may aid in the development of two-step protocols of desensitizing dentifrice application and desensitizing formulations superior to the existing calcium carbonate – L-arginine complex.

COLL 679
Evidence of stratification in binary colloidal films using microbeam small-angle X-ray scattering

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Recently, there has been growing interest in controlled stratification during multi-component evaporative film formation. Colloidal films with stratified, or layered, configurations have many useful applications, including bulk heterojunction deposition in renewable energy sources and flexible electronics, and antireflective and antibacterial coatings. Traditional deposition could be greatly improved if particle segregation could be controlled. However, particle movement in these complex systems is not well understood. We probed stratification in binary colloidal systems with different particle size ratios using microbeam small-angle X-ray scattering. By observing scattering as a function of film depth for both mixed and pure films, we determined particle concentrations at different vertical locations within the dried films using a linear combination analysis. Our results loosely agree with previously reported stratification models, as we observe three distinct stratification regimes: inverted small-on-top, large-on-top, and no stratification. Further observation of particle movement during film formation is necessary for a complete understanding of structure development.

Stacked binary film scattering data as a function of film depth, including a representative scattering detector image (left). The three major types of stratification configurations observed
are: large-on-top (right top), inverted small-on-top (right middle), and no stratification (right bottom).

**COLL 680**

**Independent control of diameter and length of silver nanowires, assembly in the form of percolative networks for transparent electrodes and advanced optoelectrical characterizations in functional devices**

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There is a market need to develop new materials for the fabrication of transparent electrodes, which are currently made of indium tin oxide (ITO). The indium scarcity associated to the lack of flexibility of ITO as well as a relatively high cost of fabrication has prompted the search for alternative materials. Among them, the use of silver nanowires appears as a potential breakthrough in this field. When used in the form of random networks, these one-dimensional nanomaterials have demonstrated remarkable ability for the fabrication of high performance transparent, electrically conductive flexible materials. They exhibit excellent performances, with sheet resistance of only few Ω/sq and optical transparency above 90%. Moreover, the fabrication of these electrodes is carried out at ambient conditions which renders this technology promising for the straightforward fabrication of various devices.

We will present how it is possible to control *independently* the length and the diameter of the silver nanowires during the polyol synthesis by fine tuning of key parameters (e.g. reactants’ concentrations and temperature), and the importance of the purification process. A focus will then be performed on their assembly on large surfaces to reach the percolation threshold, and the associated in situ optoelectronic characterizations. We will show how the optimization of the junctions at the nanoscale directly governs macroscopic performances. Complementary mapping techniques, based on infra-red thermography and one-probe electrical systems, as versatile tools for imaging network homogeneity and degradation dynamics during failure will be discussed. Integration into various functional devices will be presented and discussed.
Coll 681

DNA-programmed nanoparticle crystallization at interfaces

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The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices with unique structure-dependent physical phenomena. While DNA base pairing has enabled the development of materials with
nanometer-scale precision in nanoparticle placement and independent control over particle size, lattice parameters, and crystal symmetry, manipulating the macroscopic shape of the lattices remains challenging. By pairing this “bottom-up” assembly method with “top-down” lithographic techniques and assembling nanoparticle superlattices on a patterned substrate, complete control over crystal size, shape, orientation and unit cell structure can be realized. The key challenges in developing this technique are to first understand how different design factors affect the assembly process in this broken-symmetry system that is assembled at an interface, and subsequently develop structure-property relationships that correlate the above mentioned design parameters with the resulting overall material structure. Here, we examine both at-equilibrium deposition processes capable of generating single crystals with well-defined shapes, as well as post-deposition annealing to transform disordered particle arrangements into crystalline arrays. Using a combination of X-ray diffraction and electron microscopy techniques, both surface morphology and internal thin film structure are examined to provide an understanding of the mechanisms of particle crystallization under conditions where crystal growth is anisotropic due to a boundary condition. This novel method for controlling particle assembly draws several strong analogies to traditionally atomic epitaxy/heteroepitaxy, providing a useful tool for understanding thin film growth processes. As a result, we are able to realize 3D architectures of arbitrary domain geometry and size, thereby making materials with unprecedented precision across multiple length scales.

COLL 682

Synthesis of Janus gold nanoprisms and high yield gold nanoprism dimers in solution

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The incorporation of different coating molecules into nanoparticles provides a unique platform to generate functional building blocks for various complex and interesting applications. Janus particles, which possess asymmetric structure and more than one type of surface chemistry or functionality have attracted intense interest due to their unique structures and properties. Maximum utility of Janus particles requires judicious selections of coatings and complex functionalization techniques that impart shape anisotropy and directional interaction to the core particles. Most published works on Janus particles so far focused on applying coating molecules on isotropic particles (e.g. spheres). Here, we demonstrate a unique method to controllably coat both facets of geometrically anisotropic triangular gold nanoprisms with two distinct molecular coatings, giving rise to the formation of amphiphilic Janus gold nanoprisms. By incorporating hydrophobic hexadecane thiol coating and thiol-modified DNA (21mer) into the major flat surfaces of gold nanoprisms, we synthesize amphiphilic Janus particles which align themselves on the interface of water-chloroform mixture.
Furthermore, we also synthesize high yield of gold nanoprisms dimers by mixing two sets of Janus gold nanoprism solutions, where one facet of both sets is coated with PEG (polyethylene glycol) thiol and the other facets are coated with complementary DNAs.

Water-Chloroform mixtures containing: (Left) hydrophobic GNPlates, (Center) Amphiphilic GNPlates, and (Right) hydrophilic GNPlates

Dimer formation of gold nanoprisms

**COLL 683**

**Template-confined DNA-mediated nanoparticle assembly on surfaces**

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DNA-functionalized colloidal nanoparticles (NPs) represent promising constructs for the synthesis of higher-order materials through programmable DNA “bonds”. Using template-based approaches, these NPs can be assembled onto surfaces, allowing access to a wide variety of encoding and device fabrication applications. Therefore, a fundamental understanding of the behavior of NPs on surfaces and in confined spaces is crucial if NP superstructures with precise structural control are to be realized. We have systematically investigated the diffusion and adsorption properties of DNA-
modified NPs in lithographically-defined, high-aspect-ratio pores using template-confined, DNA-mediated assembly. Our studies allowed us to establish design rules based on pore dimensions, NP size and shape, NP concentration, solution temperature, and time for template-confined, DNA-mediated NP assembly on surfaces. Importantly, these design rules enable one to predictably and precisely place individual NPs into virtually any designed two- and three-dimensional arrangements. Hence, we foresee this template-confined, DNA-mediated NP assembly platform has immense potential for the creation of optically active metamaterials that have never before been explored.

COLL 684

Microfluidic studies of colloidal perovskite quantum dots

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Since the discovery of colloidal metal halide perovskite quantum dots (QDs) three years ago, they have rapidly grown to become one of the most promising classes of nanomaterials for applications in low-cost and highly efficient optoelectronic devices. Anion exchange reactions of the highly luminescent perovskite QDs provide a facile post-synthetic route for tuning of the absorption/emission bandgap of these exciting nanocrystals. Synthesis, screening, and optimization of colloidal QDs are conventionally conducted using time- and material-intensive flask-based approaches. Process optimization is therefore limited by the sampling rate, off-line analysis time, and batch reactor/reaction process control. Batch reactors suffer from mixing and heat transfer inefficiencies that degrade the resulting physicochemical properties of the QDs and worsen with the reaction scale.

Our group has recently developed a modular intelligent flow reactor integrated with a translational in situ spectral monitoring probe for continuous synthesis and systematic
studies of the colloidal synthesis and anion exchange reactions of perovskite QDs. Utilizing the developed flow synthesis platform, we have demonstrated, for the first time, a mixing-controlled growth kinetics of cesium lead tribromide perovskite nanocrystals. The intelligent flow synthesis platform consists of modular heating units equipped with a unique in-situ translational flow cell (UV-Vis absorption and fluorescence spectroscopy). The translational movement of the spectral monitoring probe along the tubular reactor decouples the effect of early timescale mixing of QD precursors from the residence time (i.e., growth time) along the microreactor. Automated sampling along the continuous flow reactor enables rapid photoluminescence and absorption spectra sampling across 68 ports (i.e., reaction times) spanning residence times ranging four orders of magnitude – from 100 ms to 17 min. Varying the average droplet velocity moving in the flow reactor tunes the degree of QD precursor mixing within droplets, resulting in perovskite nanocrystals with different size and optical properties. The developed flow synthesis approach enables rapid discovery, screening, and optimization of perovskite QDs with desired optoelectronic properties via high-throughput screening (>10,000 experimental conditions per day) of the accessible synthesis parameter space.

COLL 685

Monte Carlo simulation of gold nanowire self-assembly driven by van der Waals forces

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Nanowires (NWs) have a large aspect ratio and available surface area which has made them beneficial for applications in biosensors, electronic/optic devices and power storage devices. However, realization of many of these applications requires that NWs have to be positioned and oriented through an assembly process. Hence, it is essential to develop assembly strategies and techniques to achieve desired structures. Self-assembly techniques can be utilized to assemble NWs over a wide range of sizes in the absence of an externally applied driving force (i.e., fluid flow or magnetic or electric fields). In this work, we explored NW assembly using a patterned NW-substrate interaction. Experimentally, silica-coated Au nanowires (diameter 340 nm, lengths of 2.4 μm and 4.4 μm) are observed to assemble into various different patterns on parallel aligned, Au nanopads (widths of 2.4 μm and 4.4 μm), which create a series of “stripes” on a glass substrate. We develop a model of this system considering van der Waals (vdW) and electrostatic interactions among NW and vDW interactions between NW and the nanopads. Due to roughness, NW accumulate extra charge at their ends and this plays an important role in describing the assembly. Monte Carlo simulations of assembly were performed based on this model. The assembly patterns and properties for various NW agree well with experimental results. The simulations indicate that while
the patterned vdW attraction generated by the Au nanopads plays a leading role in bringing NWs onto the pads, interparticle forces dictate NW ordering on the pads.

**COLL 686**

**Synthesis and applications of chiral Au nanoparticles**

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Au nanoparticles modified with amino acids have been used as enantioselective separators of the chiral molecules. The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L-Penicillamine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide and other chiral analytes. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by their interaction with Au nanoparticles. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L-Penicillamine selectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L-Penicillamine (D-Penicillamine) selectively adsorb the R-propylene oxide (S-propylene oxide). A simple model has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-propylene oxide adsorption on the chiral Au nanoparticles.

**COLL 687**

**Controllable synthesis and shape-directed self-assembly of gold nanoarrows**

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Self-assembly of colloidal nanocrystals into complex superstructures offers remarkable opportunities to create functional devices and artificial materials with unusual properties. However, the structural complexity and tunability of nanocrystal superlattices are restricted by the limited geometries of the nanocrystals available for supercrystal self-assembly. Here we show that uniform gold nanoarrows (GNAs) consisting of two pyramidal heads connected by a four-wing shaft can be readily synthesized through controlled overgrowth of gold nanorods. The formation of the unusual GNAs may be ascribed to kinetic control coupled with selective surface passivation under the delicately controlled growth conditions. The distinct concave geometry endows the gold nanoarrows with unique packing and interlocking ability and allows for the shape-
directed assembly of sophisticated two-dimensional (2D) and three-dimensional (3D) supercrystals with unprecedented architectures. It has been revealed that the assembly structure of the GNAs is largely dependent on the concavity structures of the GNAs. Furthermore, electromagnetic simulation of the diverse nanoarrow supercrystals exhibits exotic patterns of nanoscale electromagnetic field confinement. This work may open new avenues toward tunable self-assembly of nanoparticle superstructures with increased complexity and unusual functionality.

A

B

C

100 nm

100 nm

COLL 688

Effect of crystal quality on the brilliance of structural color from self-assembled colloidal crystals

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We study and report the relationship between self-assembled colloidal crystal quality and the brilliance of structural color displayed by these crystals. Structural color has potential applications in optical materials because this color arises due to light diffraction from periodic arrays of particles; it is less prone to environmental degradation than other ways to produce color. To establish the relationship between colloidal crystal quality and the brilliance of structural color, we studied two variables using a combined experimental and computational approach. First, we quantified the relationship between
the thickness of self-assembled colloidal crystals and the brilliance of structural color as measured by reflection. Second, we incorporated dopants into the self-assembly process to probe how impurities and the defect microstructures they produce affected crystal quality and structural color brilliance. In the experiments, we assembled polystyrene microspheres into colloidal crystals with different thickness via solvent evaporation. The thickness profiles were characterized by cross-sectional scanning electron microscopy and profilometry. The spectral response of colloidal crystals measured with a white light spectrophotometer shows how the brilliance of structural color increases as a function of the crystal thickness. Additionally, we manipulated the defect structures of colloidal crystals by introducing differently sized particles as impurities. As the concentration of the impurity spheres increased, the brilliance of structural color reflection decreased. We found that impurity size determined the sensitivity of structural color brilliance to impurity concentration. We simulated colloidal crystal growth via sedimentation at various impurity concentrations using HOOMD-Blue. The reflection spectrum of defect structures was calculated using the Finite Difference Time Domain (FDTD) algorithm as implemented in Lumerical™. The simulation results were used to validate and explain the experimental results. These findings can guide the design of optical materials to tune structural color intensity.

COLL 689

Interfacial behavior between lipid films and soluble saccharides: A cooperative adsorption model

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Soluble saccharides are abundant in the sea surface microlayer and even more so in sea spray aerosols. In bulk sea water, these saccharides are present in a sub-ten micromolar concentration, but at the ocean surface these soluble sugars are enriched 1-16x fold relative to sodium. We have experimentally investigated this phenomenon using a cooperative adsorption mechanism. Cooperative adsorption describes an interaction between an insoluble Langmuir film adsorbed to the aqueous/vapor interface and soluble organics that would normally not be enriched at the surface. This interaction is studied with surface specific techniques including sum frequency generation vibrational spectroscopy (SFG-VS) and surface tension measurements. We studied the changes in biologically relevant lipid monolayers (DPPC and DMPE) in the presence of different saccharides including glucuronic acid and trehalose. These saccharides cause structural changes in the lipid monolayers indicating cooperative adsorption. Differential scanning calorimetry was used to examine changes in lipid bilayers due to the presence of these saccharides. Glucuronic acid causes DPPC’s gel-liquid crystalline transition temperature to separate into two distinct transition temperatures that both increase as a function of glucuronic acid concentration.

COLL 690
Lipid-lipid interactions in *Escherichia coli* mimetic inner membrane

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Different strategies are currently followed to eradicate bacteria, involving most of them the disruption of the bacterial membrane that ultimately cause the cell death. On the other hand, bacteria regulate their membrane lipid composition and the degree of unsaturation of their hydrocarbon chains as a response to environmental signals. The anticipation of the adapted membrane properties is of high relevance to increase the targetability of novel antimicrobial agents.

The current work engineers simple and reliable artificial membranes that mimic the *Escherichia coli* (*E.coli*) cell membrane, to anticipate the lipid-lipid interactions upon changes in its lipid composition. The high reproducibility and versatility of the Langmuir and Langmuir-Blodgett techniques make them a convenient model system to investigate the properties of such biomimetic membranes. The natural myriad of each lipid that constitutes the *E. coli* membrane (~ 77 % phosphatidylethanolamine (PE), ~ 13 % phosphatidylglycerol (PG) and ~ 10 % CL cardiolipin (CL)) is used to form biomimetic membranes constituted by several PE:lipid ratios. PE and PG establish ideal mixtures and present liquid expanded (LE) state, which could be anticipated based on their similar size and shape. Oppositely, PE and CL present also LE state but form non-ideal mixtures according to the differences in shape and size of both lipids. Both PE-lipid systems present the same physical state and minor differences in rigidity regardless the PE content in the mixture. Therefore, the changes in the bacterial membrane lipid composition may influence the membrane proteins function rather than affecting the elasticity of the bacterial membrane.

**COLL 691**

Quantification of weak and ultraweak carbohydrate-carbohydrate interactions in cellular recognition

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Controlled cell-cell interactions play a crucial role in many biological events. Some processes like embryonic development and tumor metastasis rely on these short-lived extremely weak recognition events, which demand many parallel but rather weak and thus reversible bonds but still highly specific interaction. The ultra-weak carbohydrate-carbohydrate interactions (CCIs) between glycosphingolipids provide the required adhesion force and high specificity. Here, we employ analytical methods based on atomic force microscopy (AFM) to investigate two very weak interactions, one relying on the homophilic Lewis X – Lewis X recognition and the other one between the ganglioside GM3 and the cerebroside LacCer. By combining single cell experiments and model membrane studies we were able to quantify not only the involved forces but also the extract the thermodynamics of the weak interaction between two sugar moieties.
For single cell experiments B16-F1 and B16-F10 tumor cell lines displaying different malignancy were used to investigate cell attachment by means of single-cell force spectroscopy (SCFS). A single cell is attached to a Poly-D-lysine coated cantilever and brought into contact with a LacCer containing solid supported lipid membrane (SLM). The recorded force-distance curves here deliver a direct measure of the interaction forces and adhesion energies between the GM3 overexpressing cells and the LacCer containing SLM.

Cell experiments are complemented by model membrane studies employing colloidal probe microscopy (CPM). Here, the interactions between LacCer containing SLMs and a silicate sphere coated with a GM3 containing membrane are probed. These experiments provide a direct measure of the binding affinity between the carbohydrate moieties and its dependency on the cell membrane composition and lateral bilayer organization.

COLL 692

Design of polymer-based asymmetric membranes and compartmentalized vesicles

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Polymersomes are robust self-assembled vesicular structures that are widely employed in a variety of domains from nanomedicine to artificial cell design. Control over their membrane diffusion properties and structural integrity is crucial for their future development, especially as artificial cell models. Compartmentalization in eukaryotic cells is a crucial feature that allows separation and protection of species as well as simultaneous different enzymatic reactions to take place independently in a confined space with high spatio-temporal control. A number of techniques have been developed to afford structural analogues of eukaryotic cells, namely multi-compartment systems, such as double-emulsion, layer-by-layer assembly, micro-fluidics or phase transfer of emulsion droplets over an interface. Liposomes in liposomes are the first compartmentalized systems that appeared in the literature from the initial contribution of Zasadzinski. More recently, polymeric vesosomes (polymersomes in polymersomes) were developed, especially in our group, and used as scaffolds for cascade enzymatic reactions. These complex systems both mimic the structural and functional characteristics of the eukaryotic cell and thus provide a simplified biomimetic model that can serve as a tool for the understanding and the study of the cell properties.

The mixing of different biomaterials (i.e. lipids and polymers) is a new attractive orientation that widens the use of vesicular carrier platforms for cell mimicry. Our recent developments concerning the design of multi-compartment cell-like systems composed of nano-sized liposomes or polymersomes entrapped in the lumen of giant polymersomes will be presented. We demonstrate that we can achieve controlled release of species in time and space by selectively bursting polymersomes with high
specificity and temporal precision and consequently, deliver small-encapsulated
vesicles (polymersomes or liposomes). The formation of asymmetric membranes,
resulting from the combined assembly of a lipidic and polymer layers, and the study of
their dynamic and diffusion properties will also be presented.

COLL 693

Connecting cell plasma membrane lipid oxidation to cell dysfunction in oxygen
toxicity

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Oxygen toxicity is an ongoing risk in central nervous system damage and is thought to
be involved in the development of many diseases including Parkinson’s disease and
Alzheimer’s disease. However, the molecular origins of oxygen toxicity remain
unknown. It is very likely that the components of cell membrane are the targets of
oxidation chemistry since the lipid bilayer in the membrane of neurons is rich in
unsaturated specials, which are prone to peroxidation. Recently, giant unilamellar
vesicles (GUVs) consisting of lipid oxidation products in the membrane or under
oxidative stress have been studied to show that lipid oxidation results in significant
changes to the morphology of GUVs and the properties of the lipid bilayers, including
membrane fluidity, lipid domains, permeability to small molecules, integrity, etc.
However, as a simple cell membrane model system, GUVs are inherently
limited by
their compositional simplicity, which lost the complicated lipid asymmetry and lipid
heterogeneity of cell plasma membrane. In this work, we incubate human U-87 MG
glioma cells under normobaric hyperoxia condition or with hydrogen peroxide and
evaluate effects of oxidation on cell function. More significantly, giant plasma membrane
vesicles (GPMVs), containing all major classes of phospholipids of cell plasma
membrane, are directly separated from the oxidized U-87 cells via inducing by chemical
vesiculants and employed as a cell membrane model to explore how oxidation alters the
chemistry of cell plasma membrane lipids and the plasma membrane lipid bilayer
properties, including the membrane lipid bilayer phase structure, fluidity and
permeability. This work allows us to draw direct connections between the plasma
membrane bilayer oxidation and cell dysfunction in oxygen toxicity.

COLL 694

α-Synuclein disrupts inter-membrane interactions

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a-Synuclein is an abundant protein found in the presynaptic terminal of neuronal axons but its physiological function remains unclear, even as the dysfunction of a-Synuclein is fundamentally linked to Parkinson’s. While a-Synuclein is accepted to peripherally bind to the membrane of synaptic vesicles (organelles that sequester neurotransmitters), there is increasing evidence that a-Synuclein can subsequently regulate diffusion dynamics of synaptic vesicles through an unknown mechanism. Here, we present strong evidence that a-Synuclein (at biologically relevant concentrations) disrupts inter-membrane interactions between synaptic vesicle-mimics at physiological salt and temperature conditions through a combination of synchrotron small-angle X-ray scattering and X-ray photon correlation spectroscopy (XPCS). In designing synaptic vesicle-mimics with membranes encapsulating a silica nanoparticle core, not only do we enforce membrane curvature and charge at the physiological limit necessary for a-Synuclein binding, but the high scattering cross-section of silica nanoparticles makes feasible the direct measurement of synaptic vesicle-mimic diffusivity via state-of-the-art XPCS. With increasing addition of a-Synuclein, our synaptic vesicle-mimics transition from a lower-than-expected diffusive state (with attractions most likely occurring due to charge fluctuations) to the expected Brownian diffusion of non-interacting colloidal particles. This transition is highly indicative of a-Synuclein sterically-stabilizing synaptic vesicle-mimics, most likely due to its projecting, highly-charged, unstructured C-terminal domain. In unveiling a novel, biophysical function for the C-terminal domain of a-Synuclein, we will demonstrate the effect of phosphorylation of a-Synuclein at S129, the post-translation modification most associated with Parkinson’s, and discuss how a-Synuclein may affect the super-structure of synaptic vesicles within the neuron.

**COLL 695**

**Morphogenesis of lipid domains in the presence of melatonin**

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Biological membranes are composed primarily of lipids and proteins. They contain structures ranging in length scales from microns to nanometers, all of which contribute to the membrane’s physiological functions. For instance, melatonin or N-acetyl-5-methoxy tryptamine, a hormone produced by the pineal gland, is believed to act as an antioxidant, and in regulating sleep and wakefulness [1]. Melatonin has also been shown to protect against several diseases, including cardiovascular disease, Alzheimer’s, and certain types of cancers, and readily partitions into cellular membranes [2]. Although there have been numerous membrane studies involving melatonin, studies
examining the role of melatonin in morphogenesis of phase separated systems are few and far between. Clinical trials in humans have resulted in mixed reports regarding the effects of melatonin on short-term cognitive functions. In one trial, melatonin improved verbal memory, with slight improvements in other cognitive tests [3]. Another trial showed that a single dose of melatonin enhanced memory functions during stress. As we age, our bodies make less melatonin, and melatonin production is particularly impaired in those with Alzheimer's and other dementias. However, there have been no studies that have clearly shown whether melatonin influences micron-sized and nanoscopic lipid domain morphology. Here, we will present our recent results on phase behavior of lipid domains at different length scales as resolved by both optical/fluorescent microscopy and neutron small-angle scattering. We will provide a compelling evidence for melatonin's function in stabilizing lipid domains both at high and low temperatures. Further scientific directions will be discussed.

COLL 696

Probing the translational dynamics of MAC-derived lipid bilayers as a component of synthetic cells

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A minimal actin cortex (MACs) employs a thin layer of polymerized actin that is chemically coupled to a lipid membrane. Recently, MACs have been shown to enhance the mechanical resilience of black lipid membranes containing biological nanopores, without blocking access to bulk solution. Our ongoing work explores the creation of actin multilayers and their effects on membrane dynamics. We observe a density and thickness increase following layering and cross-linking procedures. Membrane surface accessibility to bulk solution is also explored as a function of actin layering. The actin network and filament dynamics are imaged using total internal reflection fluorescence microscopy and the fluidity of the lipid bilayers is probed using fluorescence recovery after photobleaching and single molecule diffusion techniques.

COLL 697

Interface synthesis and machine learning for controlling stability and energy alignment of nanoparticles

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Controlling the stability and energy alignment of semiconductor nanoparticles is crucial for their many applications. In this talk, I will present some of our progresses in this aspect through both rational design and machine learning. As an example, when a semiconductor is in contact with an electrolyte, its flat-band potential (E_FB) is an
important quantity for determining band edge positions in photoelectrochemistry. Oxide semiconductors generally have a $E_{FB}$ shift of -59 mV in aqueous solutions when the pH is increased by one unit as a consequence of surface deprotonation. Many of the most desirable redox reactions, such as the reduction of $CO_2$ to $HCOOH$, or $2H^+ + H_2$, also show the same dependence on pH due to the involvement of protons. Therefore, pH cannot be used to tune the relative energy alignment between the electrode and the electrolytes. Through rationaly design, we have demonstrate via Mott-Schottky measurement that sensitized NiO with a membrane-inspired design of dye molecule (BH4) can decouple the pH dependence of $E_{FB}$. The $E_{FB}$ of BH4 sensitized NiO films showed little change as a function of pH, whereas less hydrophobic dye (P1) sensitized NiO and the bare NiO follow the Nernst shift with respect to pH. The protective layer arises from the hydrophobicity as well as the strong π-π interactions between dye molecules on metal oxide surface, which were identified from molecular dynamic simulations and spectroscopic techniques.

**COLL 698**

**Collapsed polymer-protected synthesis of complex nanocrystals and their arrays**

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Over the past decades, tremendous advances have been achieved in the synthesis of inorganic nanocrystals with tunable size, shape and composition. Particularly, multicomponent nanocrystals with two or more distinct components (e.g., metals, oxides and semiconductors) exhibit intrinsic optical, electronic, or magnetic properties inherited from each constituent component or new properties arising from the synergetic interactions between closely-placed (or contacted) disparate components. Despite reasonable efforts made at this frontier, there remain a grand challenge to the fabrication of multicomponent nanocrystals with high-order complexity in dispersion or on substrates. In this talk, I will present our recent progress on the use of collapsed polymers as protective layers to guide the synthesis of complex nanocrystals with controlled shape (and/or crystal orientation). In stark contrast to conventional synthesis where soluble ligands are selectively adsorbed to direct crystal growth, the site-preferential growth in our synthesis relies on the selective protection of seed nanoparticle surfaces with locally defined domains of collapsed polymers. By using this approach, we produce a gallery of complex nanocrystals and demonstrated the enhanced performance of these nanocrystals in sensing and catalysis.

**COLL 699**

**Bio-inspired approaches for the generation of multifunctional inorganic nanoparticles via responsive and reactive peptide ligands**

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Traditional nanoparticle structures covalently bind an organic ligand at the inorganic surface, stabilizing the colloidal suspension of the materials. This ligand layer can be structurally modified to optimize the final properties of the materials; however, little emphasis has been placed on engendering the materials with additional properties that arise from the ligand layer themselves. For instance, ligands could be designed that are responsive to stimuli, providing opportunities to remotely control the properties of the final materials. Our research has focused efforts on the application of bio-inspired approaches toward the fabrication of functional inorganic materials. We have recently demonstrated the ability to control nanoparticle synthesis from metal ion reduction to colloidal stabilization and the use of light activation to manipulate emergent nanoparticle catalytic properties, all through the use of peptides. Both capabilities are directed by the structure of the peptide molecule based upon its amino acid composition and arrangement that dictates metal ion reduction capabilities, inorganic material binding, and the ability of the biomolecules to change conformation once bound. To control material properties, the synthetic integration of an azobenzene photoswitch into a materials binding peptide sequence has been exploited. The resulting hybrid biomolecule retains the ability to bind noble metal nanoparticles and stabilize the materials, while also being responsive to optical stimuli for photoswitch isomerization. When the peptide is bound to the particle surface, selective light irradiation can be exploited to reconfigure the peptide ligand overlayer structure, resulting in fine tuning of the catalytic properties of the structure. Our recent studies have demonstrated that the level of catalytic control in the system is affected by the peptide sequence employed, position of the photoswitch within the peptide sequence, and the underlying inorganic material composition.

COLL 700

Ion-mediated ligand exchanges in semiconductor nanocrystals

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Controlling the morphology of colloidal semiconductor nanocrystals (NCs) remains to be a challenging task. Hot-injection growth strategies rely on a high concentration of monomers to promote particle nucleation, which tends to oversaturate the solution with reactive species. This leads to secondary nucleation events and other dispersion-broadening processes. Here, we report on monomer-deprived synthetic conditions as a bilateral strategy for tuning both the shape and the surface-ligand chemistry of semiconductor colloids. Rather than controlling the nucleation phase, the present method employs a post-synthetic treatment based on digestive ripening (DR), where small particles grow at the expense of larger ones. The feasibility of the present approach was demonstrated by observing a significant reduction in the CdSe nanoparticle size dispersion induced by high concentrations of L-type (amines) or X-type (oleic acid) ion-solubilizing ligands. We also observed that digestive ripening can facilitate complex ligand exchange processes that require restructuring of nanocrystal surfaces. In particular, the DR treatment has been shown to promote a classically
forbidden L → X ligand exchange in CdSe NCs, which was made possible due to the desorption of surface Se. Overall, we expect that the demonstrated strategy can be utilized as a simple post synthetic procedure for controlling the surface chemistry and reducing the particle size dispersion of semiconductor colloids.

COLL 701

Synthesis of trimetallic nanorods and nanoframes as electrocatalysts

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Trimetallic nanoparticles have been reported to be efficient catalysts for many reactions. We developed a general wet-chemistry method to produce Au-Cu-X (X=Pt, Pd, and Ag) trimetallic nanorods using galvanic replacement reaction with Au-Cu nanorods as the templates. The mild conditions, such as low temperature and slow injection of metal precursors, contributed to the slow galvanic replacement reaction and helped maintain the rod structure intact. The alloyed trimetallic nanorods showed enhanced catalytic activity for p-nitrophenol reduction after incorporating the third metal. In another study, Pt-Ni-Co trimetallic nanoframes were synthesized through acid etching of Pt-Ni-Co polyhedral nanoparticles at room temperature. The as-synthesized PtNiCo nanocatalysts showed a four-fold enhancement on specific ORR activity and a two-fold enhancement on mass activity compared with commercial carbon supported Pt nanoparticles.

COLL 702

Synthesis and characterization of highly branched ruthenium nanoparticles for oxygen evolution reaction

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Metal nanoparticles with branched morphology are promising for catalytic applications due to their high surface area and controlled surface structure, which enables both high activity and stability. Understanding the influence of the surface of branched nanoparticles to the catalytic performance is important to achieve active and stable catalyst. Herein, a facile method to synthesize highly branched ruthenium (Ru) nanoparticles with control of crystallinity is reported. The faceted branched Ru nanoparticles are five times more active and more stable than polycrystalline Ru
nanoparticles. The superior OER performance of faceted Ru branched nanoparticles is achieved by exposing low-index facets on the branch surface, resulting in low ruthenium dissolution rate. Our work provides an approach to design active and stable electrocatalysts that greatly contribute for the further development of OER electrocatalyst.

Low-index facets

![Graph showing electrocatalyst performance](image)

**COLL 703**

**Multilayering of α-alkyl ester sulfonate at the air-water interface**

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The α-alkyl ester sulfonate, anionic surfactants are a potentially important class of sustainable surfactants for a wide range of applications. Understanding their individual adsorption properties and the mixtures behavior along with multilayer forming at the air water interface with multivalent counterions binding is key to their exploitation. In this presentation, I will discuss the adsorption behavior of a series of α-alkyl ester sulfonate with a various of chain length from C14 to C18 and the size of the head group from methyl ester to Propyl ester to demonstrate the role and importance of the surfactant molecular structure in determining the nature of the surface adsorption in the
presence of different electrolytes and in the tendency to form extended surface multilayer structure.

**COLL 704**

**Structural coloration by cascading total internal reflection and interference at microscale concave interfaces**

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Structural color is often seen in nature because of its intense vibrancy and non-diminishing color. The ability to alter the color and optical characteristics through variations in geometric structure or material properties can lead to highly tunable or responsive coloration with applications such as displays and sensors. We describe a mechanism and design principle for creating iridescent structural color with large angular spectral separation. Light traveling by different trajectories of total internal reflection along a concave optical interface can interfere to generate brilliant patterns of iridescent structural color. This effect is generated at interfaces with dimensions that are orders of magnitude larger than the wavelength of visible light and thus, as we demonstrate, is readily observed in systems as simple as water drops condensed on a transparent substrate. We exploit this phenomenon in more complex systems, including multiphase droplets, 3D patterned polymer surfaces, and solid micro-particles, to create patterns of iridescent color that are consistent with theoretical predictions.

**COLL 705**

**Potential-induced reorganization of redox-active self-assembled monolayers in the presence of anionic surfactants**

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An odd-even effect has been observed in the apparent redox potential of self-assembled monolayers (SAMs) of ferrocenylalkanethiolates (Fc(CH₂)ₙS) chemisorbed to gold in the presence of inorganic electrolytes[1]. Recently, we noticed that this effect is reversed with the use of anionic surfactants. This project aims to uncover the origin of this inversion by investigating the reorganization of the SAMs during potential sweeps between the reduced and oxidized states when dodecyl sulfate versus perchlorate are used as the electrolyte anion. The technique used for this purpose is in-situ attenuated total reflection - Surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS), that have been previously used to document the redox-induced structural changes
occurring in ferrocene-terminated SAMs[2]. Preliminary results show an irreversible reorientation of the alkyl chains, as well as an increase in surfactant adsorption with the number of cycles.

Fig. 1. Normalized ferrocenium charge density (dashed line) and integrated intensities of $\nu_{\text{CH Arom.}}$, $\nu_{\text{CH Aliph.}}$, and $\nu_{\text{CD Aliph}}$ during anodic (open symbols) and cathodic (full symbols) potential scans. The electrolyte is deuterated sodium dodecyl sulfate.

COLL 706

Formation of surface multilayers at the air-water interface from sodium polyethylene glycol monoalkyl ether sulfate/AlCl3 solutions

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Neutron reflectivity, NR, and surface tension, ST, have been used to study the surface adsorption properties at the air-water interface of the anionic surfactant sodium polyethylene glycol monododecyl ether sulfate (sodium lauryl ether sulfate, SLES) in the presence of $\text{Al}^{3+}$ multivalent counterions, by the addition of $\text{AlCl}_3$. In the absence of $\text{AlCl}_3$ and at low $\text{AlCl}_3$ concentrations monolayer adsorption is observed. With increasing $\text{AlCl}_3$ concentration, surface multilayer formation is observed, driven by SLES/$\text{Al}^{3+}$ complex formation. The onset of multilayer formation occurs initially as a single bilayer or a multilayer structure with a limited number of bilayers, $N \leq 3$, and ultimately at higher $\text{AlCl}_3$ concentrations $N$ is large, $>20$. The evolution in the surface structure is determined by the surfactant and $\text{AlCl}_3$ concentrations, and the size of the polyethylene oxide group in the different SLES surfactants studied. From the NR data, approximate surface phase diagrams are constructed, and the evolution of the surface structure with surfactant and electrolyte concentration is shown to be dependent on the size of the polyethylene oxide group. As the polyethylene oxide group increases in size the multilayer formation requires increasingly higher surfactant and $\text{AlCl}_3$ concentrations to promote the formation. This is attributed to the increased steric hindrance of the polyethylene oxide group disrupting SLES/$\text{Al}^{3+}$ complex formation. Furthermore recent data on mixtures of SLES and sodium lauryl sulfate (SDS) in the presence of $\text{AlCl}_3$ will be presented and contrasted with the SLES alone case.
Surface phase diagram for the adsorption of SLES at the air-water interface

COLL 707

AFM colloidal probe measurements implicate capillary condensation in punch-particle surface interactions during tableting

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Adhesion of the powders to the punches is a common issue during tableting. This phenomenon is known as sticking and affects the quality of the manufactured tablets. Defective tablets increase the cost of the manufacturing process. Thus, the ability to predict the tableting performance of the formulation blend before the process is scaled-up is important. The adhesive propensity of the powder to the tableting tools is mostly governed by the surface-surface adhesive interactions. Atomic force microscopy (AFM)
colloidal probe is a surface characterization technique that allows the measurement of the adhesive interactions between two materials of interest. In this study, AFM steel colloidal probe measurements were performed on ibuprofen, MCC (microcrystalline cellulose), α-lactose monohydrate, and spray-dried lactose particles as an approach to modeling the punch-particle surface interactions during tableting. The excipients (lactose and MCC) showed constant, small, attractive, and adhesive forces toward the steel surface after a repeated number of contacts. In comparison, ibuprofen displayed a much larger attractive and adhesive interaction increasing over time both in magnitude and in jump-in/jump-out separation distance. The type of interaction acting on the excipient-steel interface can be related to a van der Waals force, which is relatively weak and short-ranged. By contrast, the ibuprofen-steel interaction is described by a capillary force profile. Even though ibuprofen is not highly hydrophilic, the relatively smooth surfaces of the crystals allow "contact flooding" upon contact with the steel probe. Capillary forces increase because of the "harvesting" of moisture due to the fast condensation kinetics-leaving a residual condensate that contributes to increase the interaction force after each consecutive contact. Local asperity contacts on the more hydrophilic surface of the excipients prevent the flooding of the contact zone, and there is no such adhesive effect under the same ambient conditions. The markedly different behavior detected by force measurements clearly shows the sticky and nonsticky propensity of the materials and allows a mechanistic description.

COLL 708

Static friction of hydrogel interfaces

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Investigating the mechanisms underlying soft-matter lubrication is pivotal in understanding the functionalities and complexities of biolubrication. Biphasic materials, such as hydrogels, are key components in multiple tribosystems in nature, including the articular and ocular lubrication systems. Inspired by these materials, we have shown that hydrogel’s frictional response is a complex combination of adhesive and viscous components originating from the elastic response of the polymer network and the viscous response of a shear thinning fluid film, respectively, during shear loading and sliding. The precise kinetic frictional response can be qualitatively and quantitatively described by the inherent microstructure of the hydrogels, the viscosity of the fluid component as well as the contact pressures at the sliding interface. However, there is still a need to investigate and quantify the wear behavior of these materials in order to understand the causation and prevention of tissue wear and damage. Current work is focused on using Atomic Force Microscopy (AFM) and the Surface Forces Apparatus (SFA) to study the possible precursors and causes of hydrogel wear when sliding under shear. Studies of the static friction by colloidal probe microscopy under a wide range of hold times, temperatures and sliding velocities have been carried out. The study will help to develop a framework delineating the relationships between contact time,
temperature and hydrogel microstructure to adhesion and static friction, and consequently wear.

**Coll 709**

*Mapping surface wetting with trifunctional organosilanes bound at the vapor/solid interface*

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Although substantial progress has been made over recent decades, the investigation of water at interfaces remains a challenge for both experimental and theoretical methods. How does the hydrophobic or hydrophilic nature of the underlying substrate affect surface wetting? Does water form a consistent, homogeneous film on surfaces such as silicon or mica? Wetting of surfaces from vapor is not uniform, the distribution of water is nonhomogeneous depending in particular on the hydrophilic/hydrophobic nature of interface. Consequently, the nature of the chemical interface drives the wetting process. With silanation, the amount and placement of nanoscopic residues of water is critical during reactions with trifunctional organosilanes such as alkoxy- and chlorosilanes. We are developing strategies to study the molecular events which occur during the surface self-assembly of organosilanes from vapor phase which focus on the role of water in forming a discontinuous hydration layer on model hydrophobic and hydrophilic surfaces. Physical experiments were designed to evaluate changes for surfaces wetted from the vapor phase with incremental increases in humidity and temperature. The studies address competition between hydrophobic and hydrophilic domains for the adsorption and coalescence of water adsorbates. The structure and dynamics of the liquid/solid interface with differences in hydrophilicity were tested using planar substrates of Si(111) and mica(0001). Changes as a function of humidity were investigated for the wetting of surfaces to assess the implications of organosilane binding through hydrolysis and condensation at designated temperature. As a unique strategy for tracking the location of water on surfaces, nanopatterning protocols with colloidal lithography furnished a means to follow the successive events of molecular assembly during the deposition and reactions of vapor-phase water and organosilanes deposited on model surfaces. Well-defined interfaces of selected hydrophilicity were prepared with exquisite control of the spacing and composition of patterned elements at the nanometer level.

**Coll 710**

*Exploration of surface cleaning and surface interactions via atomic force microscopy*

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Nanoscale thin films, such as those prepared via layer-by-layer (LbL) assembly, have become an excellent way to engineer surfaces to have specific optical, antibacterial or other functional properties. Preparing and studying nanoscale thin films require numerous surface sensitive techniques, including atomic force microscopy (AFM), quartz crystal microbalance (QCM), ellipsometry, and surface plasmon resonance (SPR), to name a few. As a result, within most studies a variety of substrates are used to fully investigate film assembly and structure. While the effect of ionic strength and pH have been studied in great detail, little attention has been given to how cleaning procedures impact the substrate and subsequent film formation. In this work we explore the how cleaning procedures such as plasma, UV ozone, and acidic piranha solution effect the surface interactions of common silicon-based substrates and what impact that has on thin film assembly and structure. Specifically, we use colloidal probe atomic force microscopy (CP-AFM) to investigate DLVO forces between freshly cleaned surfaces and colloidal silica particles (5-10μm diameter) in different NaCl concentrations (0, 0.1, 1 and 10 mM). Using these measurements, we determine the substrate surface potential and relate this to thin film properties such as thickness and surface roughness. While this work is fundamental in nature, it explores critical parameters that are often overlooked and can serve as a useful starting point from which experimental results can be compared between surface sensitive techniques and laboratories.

COLL 711

Probing the surface structure of fluorinated bottlebrush polymers with vibrational sum frequency generation spectroscopy and molecular dynamics simulations

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The molecular structure at the surface of polymer materials regulates physical and chemical properties such as reactivity, wettability, adhesion, friction, and biocompatibility. In recent years, bottlebrush polymers have gained attention in polymer research due to the ability to tune their unique architecture and functionality by tuning side chain length and composition. Bottlebrush polymers are comprised of numerous polymeric side chains densely grafted to a polymer backbone, the highly branched structure results in a steric repulsion between neighboring polymer sidechains, forcing these macromolecules to adopt a chain-extended conformation. While aspects of these polymeric structures can be characterized using standard approaches, the surface functionality and structure remain poorly understood due to challenges in selectively probing the interfacial layer. In this work we employ a unique combination of precision synthesis, molecular dynamics simulations, and surface specific nonlinear spectroscopy to elucidate the structure–property relationship of bottlebrush polymer surfaces. Using vibrational sum frequency generation spectroscopy (SFG), which is
exquisitely sensitive to interfacial ordering and local symmetry and chemical compositions, we provide new insight into the surface structure of a recently synthesized fluorinated bottlebrush polymer based on poly(2,2,2-trifluoroethyl methacrylate). SFG measurements reveal a unique molecular structure at the surface that connects the surface composition and ordering of specific functional groups with the hydrophobicity. Changes in chain length for both bottle brush and linear analogs show a change in surface structure that is in agreement with coarse grained molecular dynamics simulations. This insight into the surface composition and structure is expected to drive new advances for future applications.

COLL 712

Development of microscopy systems for the visualization of Langmuir monolayer films

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Langmuir monolayers are extensively used as models for biological interfaces and to investigate the role of membrane composition in cellular processes. Significant information can be gained from the experimental data obtained with a Langmuir trough by measuring changes in surface pressure while simultaneously reducing the molecular area under isothermal conditions. While the isotherm data and compressibility modulus provide a fair amount of information about the film, it is advantageous to visualize these films with optical microscopy systems. For this reason, Brewster Angle Microscopy and Epifluorescence Microscopy systems were constructed. Brewster Angle Microscopy is a useful technique for the analysis of surface characteristics of films at the air-water interface in a Langmuir trough due to its ability to obtain images while simultaneously collecting isothermal data, without the use of a fluorescence probe. A low-cost Brewster Angle Microscope (BAM) was constructed for the visualization of domain morphology in Langmuir monolayer films using a combination of various LEGO™ pieces and 3D-printed components in addition to a laser, a microscope objective, and a CCD camera. This was used specifically to obtain images during the compression analyses of dipalmitoylphosphatidylcholine (DPPC), dipalmitoylphosphatidylethanolamine (DPPE), as well as binary mixed monolayers of DPPC/Cholesterol. Additionally, a low-cost epifluorescence microscope was constructed using 3D-printed and off-the-shelf components for visualization of these films via the addition of a fluorescence probe. Software was developed for the manual control and automation of image processing for both microscopy systems using LabVIEW, Python, and ImageJ.

COLL 713

Multiscale approach to study molecular and interfacial characteristics of vesicles
The functions of colloidal particles are dictated by interfacial properties which are determined by an interplay of physical interactions and processes spanning multiple spatiotemporal scales. The multiscale characteristics of colloidal particles can be resolved by the hybrid Molecular Dynamics- Lattice Boltzmann technique. This technique enables the resolution of particle dynamics along with long range electrostatic and hydrodynamic interactions. We have examined the feasibility of an implementation of the hybrid technique in conjunction with a Martini-based implicit solvent coarse-grained force field to capture the molecular and interfacial characteristics of colloidal particles, such as vesicles. For simplicity, we have examined two types of vesicles whose molecular components have different sustained interactions with the solvent. One of the vesicles encompassed phospholipids and the other vesicle was composed of phospholipids and poly ethylene glycol (PEG)-grafted lipids. The molecular and interfacial characteristics of the phospholipid vesicle and PEGylated, or hairy, vesicles are found to be in good agreement with earlier experimental, computational and theoretical findings. These results demonstrate that the multiscale hybrid technique used with a Martini-based implicit solvent coarse-grained model is suitable for capturing the molecular and interfacial characteristics of colloidal particles. The results of our investigations demonstrate the potential of the combined approach in capturing multiscale interfacial characteristics of intra- and inter-colloid interactions in suspensions under different flow conditions, and their relation to molecular properties. In addition, this approach can be applied to design colloidal particles with multiscale characteristics which yield desired interactions with other colloidal particles and responses to external stimuli. Furthermore, the approach enables the adoption of other implicit solvent coarse-grained models to be used in conjunction with the hybrid Molecular Dynamics-Lattice Boltzmann technique.

COLL 714

Structures and kinetics of monodisperse platonic micelles: Part 5

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The concept of micelles was first proposed in 1913 by McBain and has rationalized numerous experimental results of the self-aggregation of surfactants. It is generally agreed that the aggregation number (N) for spherical micelles has no exact value and a certain distribution. However, our studies of calix[4]arene surfactants showed that they were monodisperse with a defined whose values are chosen from 4, 6, 8, 12, 20, and 32. Interestingly, some of the observed coincide with the face numbers of Platonic solids, thus we named them “platonic micelles”. The preferred values were explained in relation to the mathematical Tammes problem: how to obtain the best coverage of a sphere surface with multiple identical circles. The coverage ratio can be calculated and
produces maxima at , coinciding with the observed values. In the present talk, we will show that this “platonic nature” may hold for any spherical micelles when is sufficiently small. Furthermore, the kinetics of micellar formation is quite different from the conventional ones.

COLL 715

Self-assembly, rheology, and surface properties of biosurfactant-surfactant mixtures

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The global surfactant market is expected to reach $44.9 billion by 2022, of which 67% of the demand is from the personal care and detergents market. Due to consumers’ increasing awareness on product sustainability, the microbially produced biosurfactants are increasingly gaining the interest of the personal care industry as potential alternatives for traditional petroleum derived and chemically synthesized surfactants. However, prior to that, an understanding of how performance criteria such as rheology and interfacial properties are affected by substitution of traditional surfactants with biosurfactants is required. In this study, the effect of rhamnolipid and sophorolipid biosurfactants on the rheological response and interfacial properties of traditional surfactants such as sodium laureth sulfate and cocamidopropyl betaine is explored utilizing a range of advanced characterization techniques. Diffusing Wave Spectroscopy based Optical Microrheology is specifically carried out to gain insights into the short time dynamics in these systems and is also utilized for extracting wormlike micelle structural parameters such as contour lengths and persistence lengths. These insights are utilized to develop unique formulation design rules for biosurfactant based products.

COLL 716

Synergistic interaction in mixed surfactant system in presence of oil and various counter-ions: Effects on foam stability and emulsification

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A mixed zwitterionic/anionic surfactant system of N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS)/Sodium Dodecyl Sulphate (SDS) was investigated for foam stability and foamability at various molar ratios. The studies were performed in the presence of n-hexane and the effect of Na\(^+\), Ca\(^{2+}\), and Al\(^{3+}\) was investigated. Surface and interfacial tension measurements were carried out to measure the critical micelle concentration (CMC) of these surfactant systems. The interaction parameters measured the nature and magnitude of interaction between the two surfactant species in mixed micelles and in adsorption monolayer, respectively. Negative values of the interaction parameters in the mixed micelles and monolayer indicated a weak synergistic
interaction. The mixed surfactant system of zwitterionic/SDS presented a near ideal behavior. This may be due to the exclusive position of the positive and negative centers on a zwitterionic surfactant molecule. Blender test was performed for measuring the foamability and foam stability at different molar ratios for the mixed surfactant system. Our experimental results indicated the presence of counter-ions which improved the foam stability, as the binding of counter-ions between the surfactant molecules occurs which screens the charge at the foam films and Plateau borders. Foamability and foam stability were found to depend on the interaction parameters, although a systematic relation is difficult to establish. The electrical properties at the oil-water interface of the mixed surfactant system were studied using the zeta potential measurement. Emulsions were prepared at different molar ratios with \( n \)-hexane as an oil phase. A strong stability of the prepared emulsions was observed for \( \text{Al}^{3+} \) when compared to \( \text{Ca}^{2+} \) and \( \text{Na}^{+} \) as counter-ions play a significant role in the stability of these emulsions. The effectiveness of these counter-ions followed the sequence \( \text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^{+} \). Evolution of droplet size with time was investigated using dynamic light scattering (DLS) for the mixed surfactant system.

COLL 717

Tunable surfactant phase transition in the presence of additives: a deposition study

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Double tail surfactants typically assemble into lamellar aggregates in aqueous solutions. Generally this class of amphiphiles is well-known for its swelling potential.\(^1\) In this study, the effect of additives on the gel-to-liquid crystalline phase transition temperature (\( T_m \)) of dioctadecyldimethylammonium chloride (DODAC) surfactant system is determined. We have demonstrated that depending on the molecule, its location in the water phase or at
the interface, a destabilization of the surfactant structure can occur resulting in a lower \( T_m \).\(^2\) In some cases, a transition from lamellar to a reversed sponge phase is observed (Fig. 1). In this work, we answer the question on how the physicochemical characteristics of both surfactant and additive can tune the aggregate behavior. In addition, the effect of deposition and adsorption of these surfactant systems onto hydrophilic silica is evaluated. Small and wide angle X-ray scattering (SAXS/WAXS) was used to study the organization of the lamellar phase and its crystalline structure. Differential scanning calorimetry (DSC) studies provided the transition at which the “frozen” alkyl chains gain free movement due to its melted state. The observations indicate that it is possible to obtain a melted state, \( L_\alpha \) phase, at a significantly lower temperature in the presence of an additive and suggest that it is possible to achieve a liquid crystal-to-gel transition by dilution.

\[\text{Fig. 1 (i) SAXS profile and 2D image of 35 wt. \% DODAC-water binary system. (ii) SAXS profile and 2D image of DODAC-water-sodium butyrate ternary system. (iii-A) WAXS profile and 2D image of DODAC-water-butyric acid ternary system after 10x dilution; (iii-B) Thermogram under heating for DODAC-water-butyric acid; (iii-C) Thermogram under heating for DODAC-water-butyric acid after 10x dilution.} \]

COLL 718

Study of temperature-induced coacervate-to-vesicle transition of globular fusion proteins towards engineered protein vesicles

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Protein coacervates that separate from the surrounding aqueous phase have a significance in biology to understand the origin of life as well as in diverse engineering fields for many biological applications including protein delivery. Previously, we demonstrated that the recombinant fusion protein complexes, a globular domain fused with a glutamic acid-rich leucine zipper (globule-\( Z_E \)) and an arginine-rich leucine zipper
fused with an elastin-like polypeptide (ZR-ELP), self-assemble into vesicles upon heating through an intermediate coacervate phase. To engineer structural properties of the self-assembled protein vesicles, it is necessary to understand the coacervate-to-vesicle transition and control the coacervate droplets pre-assembled from soluble proteins. Herein, we investigate the kinetics of soluble-coacervate-vesicle phase transition of globule-ZE and ZR-ELP complexes by microscopy and scattering techniques at different temperatures as well as mathematical modeling for two-step protein assembly. The relative concentration of proteins pre-assembled in coacervate droplets to free soluble proteins dictates the kinetics of coacervate growth and vesicle transition. Based on the results, we identify strategies to engineer the size of globular protein vesicles by simply tuning coacervate size via growing time and temperature. This study gives fundamental and practical insights for the development of globular protein-rich colloidal materials including coacervates and vesicles for drug delivery, micro-reactors, and protocell applications.

COLL 719

Developing a data set of experimental results to support model development for simulations of the CnEm nonionic surfactants

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Our project involves the use of experimental data to drive the development of force fields suitable for industrial uses. One of the first applications of our approach is for the formulation of a force field that can be used to investigate the micellar properties and phenomena of the CnEm nonionic surfactants, which are common, industrially important amphiphilic compounds of the form H-(CH2)n-(OCH2CH2)m-OH. These are short diblock copolymers with a linear aliphatic chain constituting the hydrophobic region, and a polyether (polyethylene oxide) chain constituting the hydrophilic region.

An extensive body of experimental literature on these molecules has been created since approximately 1960, addressing their bulk properties, the behavior of mixtures in which they are a component, and associated micellar properites. However, this literature data has proven to be inadequate for the development and testing of force fields, which requires accurately measured observables relevant to the phenomena of interest (e.g., critical micelle concentrations and aggregation numbers), over a sufficiently broad range of molecules, and over a range of relevent thermodynamic variables (e.g., temperature and concentration).

We have used some data from the literature, but were required to undertake new
dynamic light scattering (DLS) experiments to help produce the required data set. This talk will review the requirements for such a data set, why they have not been met in spite of years of effort, the experimental results we have compiled and produced, and preliminary results from our use of the data to produce a useful force field for accurate computer simulations of micellar phenomena.

Our experience presents a cautionary tale for those wishing to mine the experimental literature to feed machine learning techniques.

**COLL 720**

**Heads up: Molecular interactions between surfactant head groups at an oil-water interface**

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The enhanced behaviors displayed between co-surfactants are valuable from an environmental, economical, and toxicological perspective. Working in conjunction, mixed surfactant systems can be used in lower concentration regimes and display surprising surface phenomena. The molecular interactions between surfactants with different head group charges leads to the formation of a wide variety of three-dimensional structures such as micelles, emulsions, vesicles and liposomes. The molecular properties that govern the macroscopic properties such as: shape, overall stability, and resultant applications reside at a buried oil-water interface that is difficult to exclusively probe. Using vibrational sum frequency spectroscopy (VSFS), a non-linear surface specific technique, allows for the direct measurement of the mixed system directly at the interface where their properties are most relevant. Few studies have focused on head group interactions, choosing instead to focus on the more prominent long alkyl tails, which are simpler to characterize. However our research has elucidated surprising concentration dependent behavior, which can serve as a useful indicator that provides insight about the head group packing structure. In addition, VSFS provides valuable insight into the structural orientation and packing dynamics that play a role in the competitive and cooperative effects that occur between surfactants at the oil-water interface.

**COLL 721**

**Poly: Gone! Desorption of polymer upon formation of bulk micelles**

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The interaction of charged polymers and surfactants has long been of interest due to their synergistic lowering of water’s surface tension. Their uses have been realized in cosmetics, food science, industry, and targeted drug delivery. Despite their applications, determination of the structure of surface polymer/surfactant layer has been elusive. In particular, the community has been interested in polymer adsorption (or slow desorption) at high surfactant concentration. This work focuses on the strongly interacting model system of PSS/DTAB at the oil/water interface. Surface tension and zeta potential measurements are used to follow the bulk-to-surface partitioning of complexes, while vibrational sum frequency spectroscopy reveals heretofore unseen details of the interfacial structure. Selective deuteration allows isolation of surfactant and polymer vibrational modes, providing insight into their respective interfacial structures. It was found that PSS adsorption remains relatively invariant to DTAB concentration, even through an interfacial charge inversion. However, as the surfactant concentration exceeds the cmc, complete desorption of the polymer occurs. This research answers fundamental questions about surfactant-saturated interfaces, and has applications from emulsion stability to materials synthesis.

COLL 722

Antimicrobial peptide-modified transition metal dichalcogenide nanosheets for the optical sensing of bacteria


It is of great interest to design a biosensor capable of recognizing target molecules of interest without the use of antibodies. Herein, we present an approach for the exfoliation and functionalization of transition metal dichalcogenide (TMD) nanosheets, including WS2, WSe2, and MoSe2, with an antimicrobial peptide in an aqueous solution. The resulting peptide-functionalized TMD (PTMD) nanosheets had a lateral size of 50 nm and a monolayer height of 4 nm. The PTMD nanosheets exhibited very strong Raman scattering along with a moderate intensity of fluorescence, which was used for the optical detection of pathogenic bacteria. The PTMD nanosheets were able to selectively recognize *E. coli* H7:O157 from different strains of bacteria without the use of antibodies. The binding affinity of the PTMD nanosheets was found to be higher than that of *E. coli*-specific antibody and aptamer. Finally, the PTMD sensors detected a single copy of bacterium based on their Raman scattering signals in a rapid and simple manner. This novel sensing principle could be expanded for antibody-free detection of various biomolecules.

COLL 723
Controlled fabrication of multifunctional clay/calixarene nanocomposite through ultra-fast photoinduced thiol-yne addition for an efficient heavy metal removal from industrial waste water

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Hybrid clay-based nanocomposites possess outstanding physicochemical properties which enabled their successful utilization in various applications. In this work, we present a facile approach for the preparation of hybrid multifunctional clay/calixarene nanocomposite. This is based on the reaction between thiolated bentonite clay and alkynylated calix [4]arene through the UV radical-mediated thiol-yne addition. The as-obtained nanocomposite was characterized by the XRD, XPS, DRIFTIR, and NMR. The as-synthesized multifunctional clay/calixarene nanocomposite was used for removal of both Cd and Zn from the industrial waste-water. Interestingly, the complete removal of Cd and Zn was achieved within only 40 min, owing to the unique physicochemical merits of the clay/calixarene nanocomposite. In addition to the outstanding fast and great extraction capacity of clay/calixarene, it was fully maintained without any deterioration in the activity and/or dissolving for 10 cycles.

COLL 724

Digital microfluidic applications of polymer-encapsulated quantum dot nanofluids

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Digital microfluidics (DMF) takes advantage of the electrowetting-on-dielectric (EWOD) phenomenon to independently manipulate discrete droplets (pico- to microliter) using an arrayed platform of interdigitated electrodes. Recent advances in DMF have enabled the miniaturization and automation of chemical and biochemical laboratory processes. However, there are surprisingly few reports on the EWOD behavior and DMF applications of nanofluids (i.e. engineered colloidal suspensions of nanometer sized particles), and reports of quantum dot (QD) nanofluids within such a platform are almost nonexistent. QDs have unique optoelectronic properties that arise from the confinement energy of the semiconductor nanocrystal, and have been utilized in cell labeling, displays, and photovoltaics. Herein, we report on the fundamental electrowetting behavior of polymer-encapsulated CdSe/ZnS QD nanofluids and explore their utility within a DMF platform. The stability and performance of electrically modulated QD nanofluid droplets are investigated by varying the amphiphilic solubilizing polymer,
altering the size of the QDs, and the addition of surfactants to the ambient, non-conducting medium. Optimized nanofluids are subsequently utilized within an open-source DMF platform—OpenDrop V3—to demonstrate the ability to quickly and efficiently manipulate small volumes of fluorescent liquids via an externally applied voltage. The speed of the droplets is dependent upon the voltage and surfactant employed, and the ability to mix fluids with different emissions to result in new optical properties is also presented.

![Image of droplet manipulation with voltage](image-url)

**COLL 725**

**Structured DNA and aptamer interactions with gold nanoparticle surfaces**

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Understanding the mechanism that governs the interactions in aptamer and gold nanoparticle based colorimetric assays. Gold nanoparticles (AuNPs) provide unique chemical and physical properties. The aptamer provides target recognition that induces a change in the particle stability resulting in an observable color change with the addition of salt. The interactions of aptamers and AuNPs in the presence or absence of target molecules have not been thoroughly investigated. For these assays, aptamers are physically absorbed onto the surface of AuNPs. Aptamers stabilize the AuNPs by increasing the surface charge preventing salt induced aggregation. Aptamer-target binding alters the stability of the AuNPs resulting in a color change. For these assays, single stranded (ss) DNA are known to interact more efficiently than double stranded (ds) DNA with AuNPs. The ssDNA is more efficient at preventing this aggregation. We investigated two cocaine binding aptamers in the design of these colorimetric assay type. The MN4 clone consisted of 36 DNA bases in a three-way junction. It contains multiple stems and loops. The MN6 clone has 30 DNA bases which has ss structure under the assay conditions. The initial structures were provided by Mfold, a predictive DNA folding software. Nuclear magnetic resonance (NMR) investigations confirmed these structures at 393 K (20 °C). With target added, the MN4 had small changes in structure, while the MN6 indicated no change. When analyzed with AuNPs present, the MN4 destabilized to a more ssDNA form allowing for better interaction with the AuNPs, while MN6 showed no change and remained in its ss form. When target was added,
MN4 produced the same spectra as the sample without AuNPs, while MN6 provided no change. From these investigations, we further understand the principles and mechanisms that govern AuNP-aptamer based colorimetric assays. These investigations will allow for better assay understanding and future design.

Shape-control, fluorescence functionality, and interfacial assemblies of polymer nanoparticles

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Polymer particles of well-defined tailored properties and functionalities addressing wide range of biomedical and catalysis to sensing and labeling applications. Particularly, nanoscale polymer particles are able to show unusual functions due to large surface to volume ratio compared to their bulk counterpart. In general, nanoscale polymer particles adopt spherical shape at lowest energy. In contrast, it is really a challenge, therefore, to control the non-spherical shapes of the polymer particles at nanoscale via single-step process because of their soft, flexible and amorphous chemical nature unlike metallic crystalline nature. A highly versatile reaction strategy requires to be implemented to address this challenge.

In our work, a semi-microfluidic approach combined with dynamic interfacial reaction strategy has been applied during ongoing polymerization process to address this shape-
control concern. Initially, a microreactor supports highly efficient emulsification of both immiscible liquid phases (dispersed phase and carrier phase) of the reactants. Afterward, charged polyelectrolyte-supported in-situ assembling of the growing polymer nanoparticles forms various structures of the shape-controlled polymer nanoparticles. Different shapes such as ellipsoidal to dumbbell and branched to flower-shape were produced by the application of different reaction parameters (flow rate ratio, polyelectrolyte concentration and type of polyelectrolytes). In addition, fluorescence functionality has been introduced in the polymeric network by cross-linking different fluorophores during ongoing polymerization process. Here, three different routes have been selected for making the polymeric network a fluorescence-active: (i) free incorporation of dyes in the polymer network, (ii) covalent-linking of dyes with monomers prior to the polymerization, and (iii) charged dyes on the surface of polymer nanoparticles during polymerization process. Furthermore, shape-controlled fluorescent polymer nanoparticles were used for the assembling with light-sensitive metal nanoparticles for creating active-fluoro-plasmon structure for functional applications. Here, fluorescence quenching and fluorescence enhancement effect has been controlled by control over electrostatic assembling particulate network.

**COLL 727**

**Phase transferable polymer encapsulated metallic nanoparticles**

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Polymer encapsulated nanoparticles (NPs) have potential applications in devices, biomedical nanotechnology, and catalysis. It is known that such particles retain their catalytic activity in solution as pseudo-homogeneous catalysts, effectively bridging homogeneous and heterogeneous catalysis. Here, a method to separate NP catalysts from a reaction mixture is demonstrated which involves making the encapsulating polymer phase transferable between immiscible organic and aqueous phases. Polyethyleneimine, a water soluble cationic polymer, was modified to be soluble in a water immiscible organic phase (hexane) via partial monoalkylation by reductive amination of terminal amines using aldehydes. The product has secondary amines which are protonatable to allow for shuttling between phases. Polyethyleneimine encapsulated Pt NPs were synthesized by chemical reduction and are phase transferable catalysts. These particles can catalyze both aqueous phase reactions (e.g. dehydrogenation of ammonia borane) and organic phase reactions (e.g. hydrogenation). The polymer encapsulated Pt NPs have been evaluated for activity, separation efficiency, and reuse in reactions in either phase.

**COLL 728**

**Antifouling zwitterionic quantum dot surface chemistry: Impact on intracellular diffusion**
Minimizing protein corona formation around nanoparticles by using stealth polymer is a current strategy to limit non-specific cellular uptake and to increase blood circulation time. In addition, the antifouling property is a prerequisite for specific targeting and drug delivery. PEG coating is most commonly used for this purpose but zwitterionic surface chemistry appears as an interesting alternative. The wide range of possible variations of zwitterionic materials is clearly an advantage compared to PEG but in return, the impact of the molecular design on protein-adsorption properties must be optimized. Here, we present some results about interactions between polyzwitterionic coated quantum dots and albumin or whole serum. Sulfo betaine, phosphorylcholine and carboxybetaine based polymers have been synthesized by RAFT. A terminal vinylimidazole block was added at the end of the polyzwitterion to ensure anchoring at the quantum dots surface. Hard protein corona formation was quantified after ultracentrifugation by fluorescamine assay. Fluorescence Correlation Spectroscopy (FCS) was used to characterize dynamic interactions between proteins and QDs directly. We found that sulfobetaine based polymer is able to totally prevent hard and soft corona formation with BSA and proteins of serum around nanoparticles making this polymer ideal for antifouling applications. The phosphorylcholine and carboxybetaine ligands are less efficient and induce formation of few aggregates in serum. Intracellular trajectories of individual QDs injected into Hela cells have been analyzed. The high diffusion coefficient ($D_{60ms} \sim 0.8 \text{ um}^2\text{s}^{-1}$) and the purely Brownian motion point to the remarkable cytoplasmic inertness of these zwitterionic coated nanoparticles. This enables in turn efficient intracellular targeting in live cells.

Finally, we will discuss the impact of the modification of globally neutral polyzwitterions by the addition of some negatively or positively charged monomers on protein adsorption and intracellular diffusion.

**COLL 729**

**Polymeric coating of individual lead halide perovskite microcrystals in polar solvents**

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The ionic bonding characteristics of lead halide perovskites (LHPs) cause them to disassemble rapidly in any polar solvents. This structural instability in polar solvents poses considerable challenges in surface coating of LHPs. Furthermore, the dynamic lattice disorder of LHPs makes crystalline coating nearly impossible. So far, surface
coating of LHPs has relied on the physical encapsulation of multiple LHP particles using hydrophobic polymers via sol-gel processes. Here, we report the colloidal synthesis and 3D encapsulation of single LHP microparticles using polynorepinephrine (pNE). Sonochemistry enabled us to produce colloidal CsPbBr$_3$ microcrystals in polar aprotic solvent without using any surfactants, and norepinephrine is added into the solution to form self-assembled coating (Fig. A). An 1-hr reaction at 50 Celsius generated ultrasmooth, 20-100 nm thick conformal coating on individual particles. High-resolution X-ray photoelectric spectroscopy suggests that the electronegative catechol group having lone pair electrons bind to under-coordinated Pb atoms, forming Lewis acid-base adducts. Density functional theory supports that each oxygen atom in the catechol forms bidentate binuclear surface complex on PbBr$_2$ at the surface. The coordination to defect sites passivates the surface, reducing hysteresis in photoemission. The multilayer polymers enhances the structural stability of CsPbBr$_3$ microcrystals in water by more than 100-folds. We achieved lasing of 5 μm LHP microcrystals in water (Fig. B).

**Fig. A.** a schematic illustration of sonochemical synthesis of LHPs microcrystal and pNE coating. **B.** Typical laser emission spectra of a coated CsPbBr$_3$ microcrystal in water upon nanosecond optical pumping above laser threshold. (Inset: Wide-field fluorescence images above lasing threshold).

**COLL 730**

Low temperature, polarization resolved, magneto-photoluminescence spectroscopy of individual colloidal lead salt quantum dots

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Lead salts nanocrystal quantum dots (PbX QDs, X: S, Se, Te) with their photoluminescence (PL) emission tunable from the near to mid-infrared have been attractive for their potential applications in photovoltaic and biomedical imaging as well as classical and quantum light sources operating in telecommunication bands. The band-edge exciton fine structure of these PbX QDs are expected to be more complex than the well-studied II-VI and III-V QDs due to complex interplay between 64-fold degenerated band-edge excitons and effects such as electron-hole exchange and shapes asymmetry. Unraveling the mysteries of band-edge exciton fine-structure requires lifting the spin degeneracy and brightening the forbidden optical transitions via application of an external high magnetic field.[1,2] It is also necessary to conduct this magneto-PL spectroscopy at low temperature and at the level of individual QDs to completely eliminate thermal and ensemble (inhomogeneous) broadening of spectral features. Let alone conducting such a magneto-PL study, performing a relatively simple single dot low-temperature PL study remained a challenge for PbX QDs due to factors involving fast photodegradation and slow radiative decay rate of PbX QDs, as well as the high noise level of commonly used infrared detectors. Here we report a low-temperature polarization-resolved magneto-PL spectroscopy of individual colloidal PbS/CdS core/thick-shell QDs. We were able to measure the anisotropic exchange splitting arising from the shape asymmetry of the PbS cores as well as Zeeman splitting and g factor as a function of emission wavelength. This unprecedented study is enabled by PL bleaching-free PbS/CdS core/thick-shell QDs and ultra-low noise InGaAs detector operating at liquid nitrogen temperature.

COLL 731

Formation and controlled growth of imine-linked covalent organic framework nanoparticles

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Covalent organic frameworks (COFs) are two-dimensional or three-dimensional polymers where the periodic arrangement of building blocks allow the framework design to translate directly into materials function. While these materials are typically isolated as polycrystalline insoluble powders, a major hurdle in the field is to further improve materials quality. In this regard, colloidal COFs presents an avenue for mechanistic studies in the understanding of the nucleation and growth processes of these materials. Simultaneously, while colloidal materials are more solution processable, precise shape and size control of these nanoparticles are still essential for their utility. Here we present a general approach to synthesize imine-linked 2D COF nanoparticles and control particle size by continuing imine condensation while preventing the nucleation of new particles. The method yields monodisperse, crystalline, and high-surface-area particles and is applicable to different imine-linked COFs. In situ X-ray scattering experiments observe the nucleation of amorphous polymers that crystallize via formal transimination
processes during particle growth, consistent with previous mechanistic studies conducted with insoluble powders.

**COLL 732**

**Nano-bionics: Assembly of functional metal-organic nanomaterials inside plants**

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Plants have a complex passive fluid transport system capable of internalizing small molecules from the environment, and this system offers an ideal route for augmenting plants with functional nanomaterials. A so far unexplored concept is the formation of functional materials, in situ, from precursors small enough to be passively internalized through the roots without harming the plants. Metal-organic frameworks are ideal for in situ biomineralization as they are composed of metal ions coordinated with organic ligands, and the precursors are small enough to be transported into and through plants. Moreover, MOFs have recently been shown to grow at bio-interfaces. Herein, we report the biomineralization of two types of metal-organic frameworks, Zn(MeIm)₂ and Ln₂(BDC)₃, inside a variety of plants using mild reaction conditions. Zn(MeIm)₂ was synthesized in a single step for plant clippings, while lanthanide MOFs (Eu₂(BDC)₃ and Tb₂(BDC)₃) were synthesized in a two-step process for both plant clippings and fully intact plants. Small-angle X-ray scattering and in situ synchrotron experiments helped elucidate the formation kinetics and crystal phases of the nano-biohybrid plants. Plants augmented with luminescent metal-organic frameworks were utilized for small molecule sensing, although other applications, such as sensing and photocatalysis, are foreseeable. Overall, the in situ generation of functional materials inside of fully intact plants could lead to more complex nano-biohybrid sensors and organisms augmented with superior performance characteristics.
Zwitterionic/thiol copolymers for antifouling

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Zwitterionic polymers contain cationic and anionic moieties on the same pendant group. Most widely known are sulfobetaines which are antifouling and highly hydrophilic materials that have been commonly used as coatings for surfaces either as polyelectrolyte films or bonded to other polymers. On the other hand, the adsorption by strong interactions between sulfur and gold is used as a layer assembly technique on surfaces, providing stability and preventing aggregation of nanoparticles. We have made a copolymer containing the sulfobetaine, 3-((2-acrylamidoethyl)dimethylammonio)propane-1-sulfonate (AEDAPS) and a protected thiol monomer 2-(4-vinylbenzyl)isothiouronium chloride, that after hydrolysis to the free thiol can attach tightly to gold surfaces and nanoparticles. Optimal conditions for the
synthesis of this versatile copolymer will be presented. In addition, the efficiency of the hydrolyzed copolymer at preventing aggregation of gold nanoparticles and adsorption of the protein corona will be discussed.

**COLL 734**

**Probing synthesis, bandgaps and stability of a family of Cs2AgMX6 lead-free double perovskite nanocrystals (M = Sb, Bi, In; X = Cl, Br)**

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Lead toxicity has sparked interest into alternative halide nanomaterials with properties similar to CsPbX3 perovskites. A promising alternative suggested from bulk studies is the family of double perovskites of the form Cs₂AgMX₆. Here, we report the robust and tunable synthesis of colloidal nanocrystals of Cs₂AgInCl₆ and Cs₂AgSbCl₆ via injection of acyl halides into a metal acetate solution under atmospheric conditions and relatively mild temperatures. We demonstrate the synthesis of single crystalline cubic nanocrystals of about 10 nm side length, and showcase their morphological similarities to other double perovskite structures in terms of their [200] facet termination and decoration with Ag⁰ spots. To compare the stabilities of the synthesized materials, we developed a titration assay based on the degradation of nanocrystals with amines as a proxy for degradation by humidity, which provides a quantifiable stability metric. This measurement showed that Cs₂AgSbCl₆ releases more than twice the decomposition energy compared to Cs₂AgInCl₆ or CsPbCl₃ and degrades in the presence of ca. one molar equivalent of amine, whereas the other two materials require more than a hundredfold excess. Using facile chemical titration to quantitatively determine chemical stability deepens the basic understanding of what makes materials environmentally stable.

**COLL 735**

**Quantitative understanding of aggregation-induced emission with polarized resonance synchronous spectroscopy and polarized stokes'-shifted fluorescence spectroscopy**

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Aggregation-induced emission (AIE) is one of the examples where molecular aggregation works constructively to endow the otherwise non-emissive molecule with
highly fluorescent capability. During aggregation, aggregate size and structure changes are accordingly accompanied with the variations of optical properties. However, quantitative understanding of the optical properties of AIE aggregate can be complicated by the interplay of scattering, absorption, and fluorescence. Reported herein is the quantification of scattering, absorption cross-section spectra of the assembled 1,1,2,2-tetraphenylethene (TPE) with the newly developed Polarized Resonance Synchronous Spectroscopy. Presented herein is an experimental quantification of the scattering cross-section spectrum, absorption cross-section spectrum, extinction spectrum, and fluorescence depolarization spectra of TPE. On the other hand, study of its fluorescence properties including fluorescence depolarization during assembly can be complicated by the strong scattering as aggregation proceeds. Polarized Stokes'-shifted Fluorescence Spectroscopy was employed to extrapolate the analyte fluorescence depolarization. The new technique presented should have a broad application for investigating different kinds of molecular assembly and disassembly.

**COLL 736**

**Nonphotochemical laser-induced nucleation of a “dense liquid droplet” of aqueous glycine formed by optical gradient forces**

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In 1996, Garetz et al. discovered that supersaturated aqueous solutions of small organic molecules such as urea and glycine, irradiated with intense near-infrared (NIR) nanosecond laser pulses, nucleated orders of magnitude faster than identical unirradiated solutions, and called this phenomenon nonphotochemical laser-induced nucleation (NPLIN) [1]. In 2010, Yuyama et al. discovered that thin films of supersaturated solutions of glycine in heavy water on a glass substrate, irradiated with a tightly-focused intense NIR continuous-wave (cw) laser beam, formed a new millimeter-sized liquid phase centered at the beam focus, with a much higher supersaturation than the surrounding solution. They called this new phase a “dense liquid droplet” (DLD) and attributed its formation to trapping of glycine clusters by optical gradient forces. In spite of its extremely high supersaturation, this phase did not spontaneously nucleate while the beam was focused at the solution-substrate interface, but immediately nucleated when the focus was moved to the solution/air interface [2].

In this talk, we report that the irradiation of a DLD of glycine and heavy water with a single, unfocused 0.4-GW/cm² 7-ns 1064-nm laser pulse results in the nucleation of glycine, while irradiation of the same 136%-supersaturated solution before formation of the DLD results in no nucleation. Additional features of the DLD will also be discussed. These findings have implications concerning the nature of the DLD.

**COLL 737**
Iron sulfide supraparticles as artificial viruses for gene and gene editing therapies

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Gene and gene editing therapies have been widely investigated for treatment of inherited or acquired genetic diseases. Efficient delivery of therapeutic agents has become a significant barrier in clinical applications due to the toxicity and instability of the vectors in the complex intracellular environment. Among non-viral vectors, inorganic nanoparticles (NPs) have become a popular strategy for nucleic acid delivery. Even though, NPs can condense the nucleic acids, the nanoshell geometry of viruses is advantageous for the gene/gene editing therapies cargo protection. Therefore, we synthetized iron-based inorganic nanoparticles which self-assemble into supraparticles with nanoshell geometry. We synthetized L-cysteine stabilized iron sulfide NPs in aqueous media to eliminate toxic reagents during synthesis. Careful selection of the reaction conditions such as precursor concentrations, pH level and reaction time allowed us to find a condition where iron sulfide NPs self-assemble into virus-like supraparticles. Transmission electron microscopy (TEM), TEM tomography and dynamic light scattering (DLS) were used to characterize these supraparticles for size, shape, and charge. Our results indicate that virus-like supraparticles contain continuous compartments, are positively charged (25±7.2 mV) and 74±21 nm in diameter. We loaded deoxyribonucleic acid (DNA) in the compartments during the formation of supraparticles. We tested these complexes in circular dichroism, UV-Vis spectroscopy, electrophoretic mobility shift and protection assays to confirm the encapsulation of DNA in the compartments. Since iron sulfide is a natural material, it presumably has low cytotoxicity and high biocompatibility. Supraparticles can condense DNA, protect it against degradation, penetrate through cellular membranes and facilitate endolysosomal escape in gene therapy. Therefore, development of these virus-like particles can be used as an effective cargo delivery tool for gene and gene editing therapies such as CRISPR.

COLL 738

Self-recognition introduced by host-guest complexation in charge regulated self-assembly of gamma-cyclodextrin derivative

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Self-assembly and self-recognition are ubiquitous behaviors of biomacromolecules and play significant roles in various biology process in living organism. Non-covalent
interactions is crucial in such behaviors. A feasible way to study the nature of self-assembly and molecular recognition is to build up a biomimetic system with controllable interactions. Our previous research has revealed that charged gamma-cyclodextrin (g-CD) derivatives can self-assemble into stable, hollow, single-layered, “blackberry”-type structures in polar solvents, and the sizes of the structures are regulated by the interaction between macromolecules. This phenomenon is similar to formation of viral capsids (both in morphology and kinetics).

Here, we report the study of a biomimetic system, the self-assembly of an ionic g-CD encapsulated of a charged borate cluster (B_{12}F_{12}^{2-}) in dilute solution. The encapsulated borate cluster increased the overall charges of g-CD, and subsequently changed the sizes of self-assembly structure. When g-CD with/without encapsulated borate cluster co-existed, instead of co-assemble into hybrid “blackberry”-type structures, they self-recognized each other, separately formed homogeneous “blackberry”-type structures with different sizes, which can be easily separated by centrifugation. The difference of intermolecular electrostatic interaction governs the sizes of “blackberry”-type structure and self-recognition behavior. We believe this study will provide a new sight on self-assembly and self-recognition.

COLL 739

One-dimensional carrier confinement in excitonic nanoshells

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We report on the synthesis and spectroscopy of energy-gradient nanostructures that support the formation of two-dimensional excitons in the shell domain. The developed geometry places a wide-gap semiconductor (CdS) at the core of the composite nanoparticle in order to funnel the photoinduced energy into the low-gap CdSe surface layer. As a result, the quantum confinement is achieved in nanoparticles which total size exceeds the exciton Bohr radius. The formation of excitons in the CdSe shell layer was manifested through a size-tunable emission and the characteristic step-like absorption profile. We expect that the developed nanoshell architecture could potentially be extended to a broader range of semiconductors (e.g. CdS/PbS, ZnS/CdS) facilitating the development of quantum confined solids offering improved charge transport characteristics.

COLL 740

Biexciton dynamics in CdS/CdSe/CdS nanoshell quantum dots

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The Auger recombination represents a significant obstacle for the prospective utilization of semiconductor nanocrystals in a variety of emerging applications, including quantum dot lasers and multiple-exciton generation (MEG) solar cells. Here, we demonstrate that the non-radiative Auger decay of biexcitons becomes suppressed in two-dimensional nanoshell quantum dots utilizing a quantum-confined layer of CdSe, which is sandwiched between a spherical, bulk-like CdS core and a surface-passivating CdS shell. The resulting double-barrier CdS/CdSe/CdS nanoshell geometry allows reducing Coulomb interactions underlying the Auger decay by enhancing the volume occupied by the confined carriers. This leads to increased biexciton lifetimes, as was demonstrated in this work through ultrafast measurements of excited state populations. In particular, we observe that the average lifetime of biexcitons in CdS/CdSe/CdS nanoshells was increased more than ten-fold as compared to zero-dimensional CdSe NCs. The shell-localization of photoinduced holes underlying the suppressed Auger decay in CdS/CdSe/CdS nanoshells was also responsible for non-radiative surface recombination of carriers, indicating that further improvements in the surface passivation strategy could result in the additional enhancement of the multi-exciton emission yield.

**COLL 741**

**Metal amidinate precursors for general solution-phase synthesis of intermetallic nanocrystals**

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Nanocrystalline intermetallic compounds show promise in several applications, however chemical methods giving phase purity and size control are lacking. Using metal precursors previously developed for atomic layer deposition but rarely explored for solution-phase materials synthesis, we demonstrate the synthesis of several phase-pure transition metal alloys including the full library of MSn₂ and MSb (M = Cr, Mn, Fe, Co, Ni) with control over phase and stoichiometry, several of which are reported for the first time in nanocrystalline form. For stannides, the synthesis of which occurs above the melting point of Sn, the alloys formation progresses via an intermediate stage of small Sn⁰ nanocrystals stabilized by the strongly-binding amidinate ligands with subsequent diffusion of transition metal atoms into tin. We find that for metals with higher melting temperatures than Sn (such as Sb), the reductant injection temperature determines the phase purity of the intermetallic product. Temperature-dependent magnetic properties of the intermetallic nanocrystals have been studied, and the effect of annealing the nanocrystals at high temperatures on crystallinity is also explored.

**COLL 742**

**Intrinsic exciton photophysics of PbS nanocrystals revealed by low-temperature single dot spectroscopy**
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With a tunable size-dependent photoluminescence (PL) in the wide infrared wavelength range, lead chalcogenide nanocrystal quantum dots (QDs) have attracted great scientific and technological interests. Yet the investigation of intrinsic exciton photophysics at the single QD level has remained a challenge due to factors involving fast photodegradation and slow radiative decay rate of this type of QDs, as well as the high noise level of commonly used infrared detectors. Herein we present a comprehensive study of the PL and polarization properties for individual core/shell PbS/CdS QDs conducted over the temperature range of 4 – 300 K. Our cryogenic (4 K) spectroscopy experiment provided a direct measurement on the intrinsic linewidth and shape of single dot PL emission. In contrast to the sub-meV narrow spectral linewidth observed for the conventional CdSe QDs, PbS/CdS single QDs are characterized by broad intrinsic linewidths of 8 – 25 meV with an average of 16.4 meV, providing a direct evidence for the predicted broad homogeneous linewidth. A broad low-energy side emission attributable to multiple phonon assisted transitions involving LO$_\Gamma$, LO$_X$ and acoustic phonon modes were also observed. By tracking single QDs from 4 K to 250 K we were able to probe a temperature-dependent evolution of emission energy, linewidth and lineshape of single QD PL. Polarization-resolved PL imaging revealed the evidence of 3D emission dipole in contrast to the 2D dipole of CdSe QDs.

COLL 743

Structural transformations of functional nanoparticles

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Novel materials with new properties are often realized by modifying their structures of existing materials without altering their composition, and one of the approaches is to apply high pressure to a material. In this talk, I will show how to take advantage of one scaling law - nanoparticles as single structural domains to investigate PbTe nanoparticles by high-pressure method. Reversal of Hall-Petch effect concerning the structural stability to particle size was first reported on PbTe nanoparticles. Based on this novel observation, the pressure-dependent amorphizations on 5 nm PbTe nanoparticles was further utilized to harvest the metastable amorphous PbTe nanoparticles of great technological applications. Then, I will also talk about how to use pressure to engineer the bandgap of photovoltaic perovskites. Finally, the phase engineering of metastable Au nanostructures is also delicately achieved and the atomic transition path is revealed.

COLL 744
Crystal structure and optical properties of the smallest piece of metallic gold: Faradaurate-279

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The discovery of smallest piece of metallic gold nanocrystal protected by 4-tert-buty1benzenethiolate characterized by single crystal X-ray crystallography, steady state and transient absorption, time-dependent density functional theory (TDDFT) and density of states (DOS) studies are reported here. Au²79(SPh-tBu)₈₄ has been named Faradaurate-279 (F-279) in honor of Michael Faraday’s (1857) pioneering work on metal nanoparticles. F-279 has a 2.2 nm diameter core-shell structure containing an Au²₀¹ truncated octahedral core (Au@Au₁₂@Au₄₂@Au₉₂@Au₅₄) with bulk face-centered cubic like arrangement, further protected by 48 Au atoms. Au²₄⁹ core is protected by three types of staple motifs, namely: 30 bridging, 18 monomeric, and 6 dimeric staple motifs. X-ray diffraction study based heavy atoms formula (Au²₇₉S₈₄) of F-279 was independently verified by Electrospray ionization - mass spectrometry and the molecular formula with the complete ligands was established as Au²₇₉(SPh-tBu)₈₄. F-279 is the smallest identified gold nanocrystal to exhibit surface plasmon resonance (SPR). It exhibits a SPR band around 510 nm. Power-dependent bleach recovery kinetics of F-279 suggests that electron dynamics dominates its relaxation and it supports plasmon oscillations. TDDFT and DOS studies with different tail group residues (-CH₃, -Ph) revealed the important role played by the tail groups of ligands in collective oscillation.

COLL 745

Optical spectroscopy of plasmonic aerosols

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Plasmonic nanoparticles are well known for their coupling and concentration of light to the nanoscale regime. Many remote sensing and medicinal applications require these nanoparticles to be both airborne and monodisperse in nature. However, plasmonic nanoparticles are typically confined to substrates or dilute suspensions and little is known for how to efficiently aerosolize or measure their properties. Here, we report on the generation of gold nanorod aerosols and characterize their optical properties. We show by controlling the nanorod aspect ratio through colloidal synthesis, the absorption peak can be tuned over 6,000 nm from the visible to the mid-infrared wavelengths in air. We find that nanorods with high aspect ratios (40 or higher) are incredibly sensitive to
their environment and demonstrate sensitivities above 4,000 nm per refractive index unit. Functionalization methods are also introduced that help prevent aggregation upon aerosolization, particularly for shorter aspect ratio nanorods. Ultimately, this work establishes a new phase for plasmonic materials, potentially enabling exciting opportunities for fundamental and applied research.

**COLL 746**

**Controlled intra-particulate surface cross-linking synthesis of multi-color carbon dots from a single source**

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We disclose for the first time, a facile synthetic methodology for the preparation of multi-color carbon dots (CDs) barring any chromatographic separations. Our results demonstrated that simple intra-particular crosslinking of surface abundant carboxylic acid groups may control photoluminescence of CDs and have been further confirmed via spectroscopic studies such IR, XPS, fluorescence spectroscopy results as well as from confocal microscopy studies. Furthermore, biological studies show that heavy cross-linking at the nanoscale surface consequently prevents its internalization into the cells via any of the investigated endocytosis routes.

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Schematic representation of the process for the preparation of multicolor carbon dots (CDs) from the D-glucuronic acid by crosslinking the nanoscale surface. Heavily and lightly ‘crosslinking’ lead to blue and green PL emission of the CDs, respectively.

**COLL 747**
Single-step hybrid nanocoating on contact lenses to face associated conditions and discomfort

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Well-performing contact lenses (CL) provide good comfort, physiology and handling, which are achieved through a combination of material characteristics, CL design and manufacturing process. At present, nearly 150 million worldwide use CL and 25% of them report discomfort. In more than 50 % of these cases, people stop or discontinue using CL for this reason. The most common causes for discomfort are: insufficient wetting, lubrication and protein adsorption on the ocular surface and a fear of, or history of eye infections. On the other hand, the eye is subjected to oxidative stress and presents a robust antioxidant defence system. However, deficiencies or alteration of this system may contribute to pathogenic eye conditions.

The current work reports on a single-step sonochemical coating of CL with ZnO nanoparticles (NPs), gallic acid (GA) and chitosan (CS). ZnO NPs represents the main antimicrobial contribution to the CL coatings and GA contributes simultaneously to the corneal antioxidant and antimicrobial defence system while CS imparts enhanced wettability and antimicrobial properties, all of them ultimately increasing the comfort of the coated CL. The ternary composite (ZnO NPs, GA and CS) coating presents high antibacterial efficiency (> 4.5 logs reduction) against *S. aureus* causative of CL-related conditions, high antioxidant capacity (≈ 95%) and maintains good biocompatibility (> 72 %) with human cell lines. The obtained multi-functionality on the CL did not affect their geometry and refractive properties.

**COLL 748**

Direct thermodynamic investigation of CdSe quantum dots & their ligand exchange interactions using isothermal titration calorimetry

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As likely the most well-studied colloidal quantum dot system, CdSe QDs are a good model with which to develop new techniques for probing surface interactions in solution phase. Though CdSe and CdSe-based core/shell QDs with native ligand coatings can show high fluorescence quantum yield and may be suitable for some applications, a detailed profile for nanoparticle surface composition and thermodynamics will be essential if QD-based technologies are ever reach their full potential. Isothermal titration calorimetry (ITC) is a sensitive and quantitative technique for probing reactions in the solution phase that has seen extensive use in biochemistry for investigating ligand-macromolecule interactions. Recently, ITC has received increasing attention as a means to study QD-ligand system interaction and dynamics. Beginning with a highly
reproducible purification technique established in our lab for a consistent QD starting material, this presentation will highlight our group’s most recent results investigating several characteristic ligand association/exchange reactions in the ITC. Through the use of ITC we have been able to elucidate effects of the solvent on key QD-ligand dynamics as well as binding phenomena responsible for large changes in QD optoelectronic properties.

**COLL 749**

Iron-oxide nanocomposites for ice nucleation and environmental remediation

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Nanoparticles are ubiquitous in the atmosphere and are known to be of the utmost importance by both health and climate organizations. Nano particle induced ice nucleation microphysical processes are recognized to be of great value in forecasting the level of the Earth’s climate change. We synthesized kaolin-maghemite-HgCl₂ composite, as one of a highly efficient and novel ice-nucleating material. A kaolin-iron oxide composite (KaFe) was synthesized to have efficient and instantaneous reactions with aqueous mercury salts. Only HgCl₂, among the different mercury salts, reacted with KaFe and generated highly efficient ice nuclei HgKaFe. When added to water, HgKaFe froze within narrow and significantly warm temperatures (− 6.6 degree C to − 4.7 degree C). To understand the mechanism of the mixed cloud formation via immersion freezing, we executed number of experiments using a suite of complementary techniques, at various levels of radiation intensity, temperature, pH, emerging metal oxides, natural & anthropogenic gases (NO₂ & O₃) for KaFe in the context of ice nucleation microphysics. We also disclosed a novel, cost-effective, instantaneous and sustainable technology for mercury recycling, with the maximum observed Hg uptake capacity using the great affinity of KaFe with Hg(II). The reduction of Hg(II) to Hg(I) by the nano-trap KaFe and Hg(I) to Hg(0) by Fe granules were the key driving forces behind such process of recycling. This study opens a door to broaden the field of effective ice nuclei for a wide range of compounds, never considered as ice nuclei until now, expanding the understanding of cloud formation & climate change. Furthermore, these new materials may likely serve as efficient sustainable materials for mercury remediation.

**COLL 750**

Use of oleophilic magnetite nanoparticles as efficient sorbent for water contaminants

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Production, transportation, and handling of petroleum and its products lead to a steady contamination of oceans and drinking water sources with hydrocarbons (HC) due to minor incidents and major disasters. To date, sufficient methods for the economically efficient and – in particular – thorough remediation of these pollutants from water are missing.

As a sustainable alternative to state of the art oil spill response methods, we present an HC sorbent based on magnetite nanoparticles (NP), functionalized with alkylphosphonic acids (PA). That functionalization renders the hydrophilic NP hydrophobic and oleophilic. This oleophilicity, in combination with the large specific surface area, eventuates in highly selective and efficient adsorption of HC on the NP surface. Thanks to their superparamagnetic nature, soaked NP can be extracted easily by an external magnetic field. Due to the strong grafting of the PA on metal oxides and its excellent stability, the presented sorbent can be reused after washing in multiple successive extraction cycles without degradation. Consequently, it enables for a full loop extraction process.

Another major pollutant of oceans are microplastics. We found that our presented sorbent is capable to adsorb to nano- and microplastics of different size and composition dispersed in the water column. After sorption, the microplastics can be easily collected in a similar manner as the HC.

Summarizing, we developed a tool to combat efficiently and selectively two of the major pollutants present in oceans nowadays.

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Fig. 1: a) schematic of the extraction process and b) extraction rates of ten successive extraction cycles.
Potent method of extracting glyphosate from water using superparamagnetic nanoparticles

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A simple and potent extraction method for the suspected herbicide glyphosate from artificial and real water samples was demonstrated. Dedicated to the unique combination of phosphonic acid and carboxylic acid binding motif, glyphosate can covalently bind instantly on the superparamagnetic iron oxide (Fe₃O₄) nanoparticles, which then can be collected from water by an external magnetic field. The glyphosate binding on the nanoparticle surface was analyzed by infrared spectroscopy, thermogravimetric analysis, and dynamic light scattering, while the binding mechanism was investigated with molecular dynamics simulations. Moreover, the effective extraction of the glyphosate was examined with liquid chromatography-mass spectrometry. From both experimental and theoretical results, approximately 2.7 molecules/nm² bind onto the Fe₃O₄-surface and can be extracted with a permanent magnet. The extraction yield in most cases was below the strong European maximum permissible value of 0.1 µg/L, independent of treating artificial or real water samples and even in competition to other contaminants. The Fe₃O₄ nanoparticles can be recycled by thermal treatment, enabling a cost-efficient full-loop process.
Preparation of pure and decorated metal oxide materials for energy-environmental applications using novel physical deposition methods and their characterization

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Changes in the global climate, especially noticeable by recent storms and significant weather variations, have led to an urgent need to understand if and/or how these changes are related to CO₂ and methane emissions. In concert with understanding this relationship it is incumbent on the scientific community to discover and develop more sustainable and efficient ways to produce and store energy. Because of their abundance and broad range of optoelectronic and physicochemical properties, metal oxides (MOs) offer a unique opportunity to address these energy/environmental challenges. Our research activities are focused on the study of pure and decorated nanoscale particles of magnesium (MgO) and zinc oxide (ZnO) and their applicability to optoelectronics, catalysis, gas separation/storage and anti-fungal/bacterial properties. The MOs we employ are synthesized using patented and novel approach which produces chemically and size selective particles. These particles can be subsequently
decorated using an innovative physical vapor deposition (PVD) process that is used to deposit atomic clusters of copper, nickel and cobalt on MgO and ZnO. X-ray powder diffraction, photoluminescence (PL), and diffuse reflectance spectroscopy have been used to examine the structural and optoelectronic properties of the bare and decorated materials. Diffraction data clearly show the emergence of ordered metal structures on the MOs; while PL results indicate a potential modification of the emitting sites on the surface. Electron microscopy and photoemission studies to determine the microscopic character of these powders are soon to be performed, as a means to fully understand the properties of the decorated materials.

COLL 753

Surface reactions of atmospheric species on amorphous zirconium hydroxide and hydroxylated titanium oxide from cluster models

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Adsorption and reactivity of atmospheric species such as carbon and sulfur dioxides can suppress surface reactivity of transition metal oxides and hydroxides. In this presentation, I will describe density functional theory simulations of surface reactions of water, carbon dioxide, and sulfur dioxide on amorphous zirconium hydroxide and hydroxylated titanium oxide nanoparticles, including formation of carbonates and sulfites. In these simulations, structure optimizations involving numerous, randomly generated adsorption configurations are combined with cluster models that mimic edges of Zr(OH)₄ particles and interfaces between nanoparticles in TiO₂ aerogels. Predicted structures, binding enthalpies, and infrared absorption spectra will be discussed.

Lowest-enthalpy structures describing different motifs of CO₂ binding on Zr₉(OH)₃₆ ● 4H₂O. Zr atoms are shown in cyan, O atoms in red, C atoms in gray, and H atoms in white. Values shown in parentheses are binding enthalpies computed with respect to separated CO₂ and Zr₉(OH)₃₆ ● 4H₂O.

COLL 754
Orientation of CdSe nanoplatelets for advanced magneto-optical characterization

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Colloidal, quasi two-dimensional nanomaterials termed nanoplatelets (NPLs) exhibit remarkable optical properties that arise from their anisotropic structure that features quantum confinement along only one dimension. Though leveraging these properties for improved devices requires oriented assemblies, very few studies have investigated routes to controlled orientation. The ability to precisely manipulate NPL orientation would also allow for meaningful studies of optical, magnetic, and electronic properties of NPLs to be implemented, the results of which would otherwise be very difficult to interpret.

Here, we achieve orientation of CdSe NPLs through two methods that are evaluated via transmission electron microscopy and small angle x-ray scattering. First, CdSe NPLs are embedded into polymer films and stretched biaxially to induce “face-down” orientation of NPLs in the plane of the film. Alternatively, NPLs can be oriented into either a “face-down” or “edge-up” configuration via a Langmuir-Blodgett type approach, in which a dispersion of NPLs in alkanes is dropcast onto an antisolvent of controlled polarity.

We apply our methodology to the preparation of oriented films of CdSe NPLs for magneto-optical characterizations focused on exciton spatial extent. Given the lack of lateral quantum confinement in a NPL, it is unclear whether the exciton is laterally delocalized, or if the strong quantum confinement induced by its thin dimension leads to a localized exciton. The spatial extent of the exciton is crucial to arriving at an understanding of NPL behavior, such as how rates of electronic processes scale with dimension. By tracking the shift in exciton energy as a function of magnetic field up to 60 T, the in-plane exciton radius can be deduced. We find that despite the common assumption that the exciton is spatially delocalized in the plane of the NPL, the exciton appears largely spheroidal. This work follows similar studies of exciton spatial extent in monolayer transition metal dichalcogenides and provides clear insight into the spatial extent of excitons in these promising, highly processible and scalable, two-dimensional materials.

COLL 755

High-temperature crystallization of nanocrystals into three-dimensional superlattices
Fast development of colloidal chemistry has enabled the synthesis of monodisperse nanocrystals with controlled sizes, shapes, and structures. The well-defined nanocrystals can be used as building blocks to create ordered superstructures with emergent functionalities through bottom-up approaches. These approaches often rely on carefully controlled assembly of pre-synthesized nanocrystals at low temperatures. In contrast to conventional approaches, this talk discusses the rapid growth (within seconds) of face-centred-cubic three dimensional nanocrystal superlattices during colloidal synthesis at high temperatures (more than 230 °C). Using in situ small-angle X-ray scattering, we observe continuous growth of individual nanocrystals within the lattices, which results in simultaneous lattice expansion. Thermodynamic models demonstrate that balanced attractive and repulsive interparticle interactions dictated by the ligand coverage on nanocrystal surfaces and nanocrystal core size are responsible for the crystallization process. The interparticle interactions can also be controlled to form different superlattice structures, such as hexagonal close-packed lattices. These results demonstrate a new type of nanocrystal interactions during colloidal synthesis and provide new insights into assembly of nanocrystals into superstructures for different applications.

COLL 756

Self-assembling of neutral and charged nanoparticles into core-shell nanohybrids with size control

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Core-shell structures of nanoparticles have wide applications in areas of catalyst synthesis, drug delivery, bio-imaging, environmental remediation, etc. The structure and the size of the core-shell play important roles in governing the physical and chemical properties of the formed nanohybrids. In this study, the core-shell structure was formed through spontaneous heteroaggregation between neutral nanoparticles (i.e. hematite nanoparticles or HemNPs) and charged nanoparticles (i.e., polystyrene nanoparticles or PSNPs). The pH of the 1 mM NaCl dispersant solution was adjusted to 6.34 so that HemNPs were neutral and underwent favorable homoaggregation whereas PSNPs were negatively charged and underwent no homoaggregation. When the two types of particles were mixed, homoaggregation of HemNPs and heteroaggregation between HemNPs and PSNPs took place simultaneously, forming HemNPs-PSNPs heteroaggregates. The size of heteroaggregates increased initially and became stable afterwards, as shown by the hydrodynamic diameter measurement using dynamic light scattering (DLS). The transmission electron microscopy (TEM) images of
heteroaggregates at the stable stage show that HemNPs and PSNPs formed core-shell structure in which HemNPs are the cores and PSNPs are the shells. The size of the core-shell nanohybrids can be controlled by varying the concentration ratio of PSNPs to HemNPs. The elevated concentration of PSNPs reduced the size of the colloidal stable nanohybrids due to that PSNPs could quickly surround HemNPs before the HemNP had the chance to attach to other HemNPs. Decreasing the concentration of the PSNPs resulted in larger size of stable nanohybrids because HemNPs could attach to each other through direct contact or bridging by an intermediate PSNP. The influence of size of charged nanoparticles on the formation of core-shell nanohybrids will be discussed as well.

COLL 757

Probing crystal growth of gibbsite and boehmite nanocrystals

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Boehmite (γ-AlOOH) and gibbsite (α-Al(OH)₃) are important archetype (oxy)hydroxides of aluminum in nature that also play diverse roles across a plethora of industrial applications. As a consequence, highly precise synthesis of these pure phases with controlled particle size, shape and properties towards an end of tunable chemical behavior is an important ongoing research and development enterprise. In addition, they are prominent components in high-level nuclear waste stored in large quantities at the Hanford Site, Washington with future processing plans dependent on developing a predictive understanding of crystal growth of these two materials. However, mechanisms of crystal growth of these minerals still remain poorly understood, particularly in the complex environment of concentrated sodium hydroxide at low water activity. In this work, magic angle spinning nuclear magnetic resonance (MAS-NMR), high resolution atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman, X-ray absorption spectroscopy (XAS), high resolution powder X-ray diffraction (XRD), and X-ray Pair Distribution Function (PDF) techniques were conducted to investigate the crystallization of gibbsite and boehmite nanocrystals. By focusing on understanding the role of aluminum coordination change dynamics from tetrahedral in solution to octahedral in solids and vice versa, and the intermediate pentacoordinate state, some unifying principles governing these transformation emerge, which are of importance for developing new methods to morphology and size controlled synthesis of boehmite and gibbsite nanocrystals and also are critical to proposal reliable techniques to manage the aluminum based minerals in nuclear waste.

COLL 758
Reversible aggregation of covalently cross-linked gold nanocrystals by linker oxidation

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The demonstration of stable alkanethiolate-capped colloidal gold nanocrystals launched a wave of research on surface functionalization strategies to control the assembly of plasmonic metal nanocrystals (NCs). One basic degree of control is the ability to reverse the NC aggregation process using an external stimulus. Reversibility is interesting because it allows for dynamic tuning of the aggregates, real-time response to stimuli, resetting of the NC assembly to its initial state, and reuse of the NCs. Current approaches rely on non-covalent interactions, including hydrogen bonding, solvophobicity, electrostatic and van der Waals forces, and π-effects. A general method for reversible self-assembly of covalently cross-linked Au NCs has not been demonstrated.

In this talk, I present the reversible assembly and disassembly of dithiol-linked aggregates of Au NCs by selectively converting the strongly-bound thiolate anchoring groups to weakly-bound sulfonate groups using ozone. Ozone has been previously used to induce reversible shifts of the LSPR of Au NCs, and to oxidize organic ligands from colloidal and surface-supported Au NCs. We show here that ozone depolymerizes the NC precipitates by converting the dithiol linkers to weakly-bound disulfonates that exchange with free citrate in solution to yield dispersions of citrate-capped NCs. The process works with all dithiol linkers we tested, including oligo ethylene glycol and alkane dithiols of various lengths and water solubility. The NC size and shape distribution is preserved. Complete redispersion of “hard crashed” bulk NC precipitates occurs with shaking at room temperature or assistance from sonication. Disassembly of colloidal aggregates formed by adding a different amount of dithiol takes seconds to days. The precipitation-redispersion cycle can be repeated multiple times by sequential addition of dithiol linker and ozone. Ozone-mediated linker oxidation is a simple, clean, and general approach to the reversible assembly of covalently cross-linked Au NCs. Interesting future directions include using smaller, more controlled ozone doses to stop rather than reverse the aggregation of Au NCs and extending this approach to Ag NCs, which may require a milder oxidant than ozone.

COLL 759

Base side of noble-metal clusters: An efficient route to exceptional captamine-protected gold, \( \text{Au}_n(\text{DMAET})_p \), \( n = 25 - 144 \)

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Magic gold nanoclusters ($\text{Au}_{25}$, $\text{Au}_{38}$, $\text{Au}_{67}$, $\text{Au}_{102}$, $\text{Au}_{144}$) are conventionally synthesized using neutral or anionic terminated thiols such as alkanethiols, 2-phenylethanethiol, glutathione, or mercaptocarboxylic acids. However, fully cationic nanoclusters have been less explored due to the difficulty of synthesis and ligand exchange. Amino-terminated gold nanoclusters have long been applied in biomedical research, but these were based on the old gold-phosphine class. Herein, we report for the very first-time one step synthesis and direct infusion positive mode ESI-MS and UV-Vis characterization of high yield and highly stable tertiary amine (2-Dimethylaminoethanethiol) protected magic gold nanoclusters, [$\text{Au}_{25}$(DMAET)$_{18}$]$^+$ and thermodynamically controlled synthesis of [(Au$_{144}$(DMAET)$_{60}$]$^+$.

**COLL 760**

**Coupling radio- and photo-luminescent emitters in crystalline colloidal arrays**

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X-ray radiation exhibits diminished scattering and a greater penetration depth in tissue relative to the visible spectrum and has spawned new medical imaging techniques that exploit x-ray luminescence of nanoparticles. The majority of the nanoparticles employed in this field utilize metals with high atomic numbers and pose potential toxicity effect. The current effort presents a general strategy for the preparation of a fully organic x-ray radioluminescent colloidal platform that can be tailored to emit in the visible spectrum through a judicious choice in donor/acceptor pairing and multiple sequential Förster resonance energy transfers (FRETs). Utilizing 100 nm particles that are doped with anthracene as the scintillating molecule which “pumps” subsequent FRET dye pairs results in emissions from ca. 400 nm out to ca. 775 nm. The particles could be self-assembled into long-range ordered arrays, and the luminescence of the particles could be dynamically tuned by coupling the observed rejection wavelength with the particles’ emission.

**COLL 761**

**Towards precise control of colloidal plasmonic nanoparticles: Synthesis and surface engineering**

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In recent years, nanoparticles have ignited people’s enthusiasm with their remarkable properties and far-reaching applications which are size, shape and composition dependent. Although a variety of nanoparticles have been synthesized in solution, the current synthetic strategies are still far from ideal, requiring more effort for precise
control which has been emerging as a new frontier in nano research. In this talk, I will present our recent work on how to realize the precise control on colloidal plasmonic nanoparticles (CPNs), including the precise control of size and shape of CPNs in colloidal synthesis with a better understanding of the reaction mechanism, and the precise control of surface engineering of CPNs through regioselective surface encoding strategy. The precise control in nano research is of critical importance to understand the structure-property correlation, customize the CPNs synthesis and surface engineering for specific applications. Its realization will be accompanied by a better understanding of mechanism, the development of synthetic and surface engineering technology and provide many exciting opportunities for discovering new applications.

COLL 762

Effect of pH on the synthesis of monodispersed gold bipyramids with finely tunable LSPR peaks

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Gold (Au) bipyramid (BP) has consisted of two pentagonal pyramids that share a base, which pentagonal pyramid consists of five equal angularly faces sharing edges. The most interesting performance of Au BPs is their high mono-dispersity and then enhance homogeneous spectral narrowing for the plasmon peaks. In addition, Au BPs have more chemically stability than Au nanorods, possess a larger figure of merit value and higher sensitive refractive index than Au nanorods. Thus, local electric field enhancements of Au BPs are multiple times larger than Au nanorods. Therefore, Au BPs have attracted the most attention recently. However, the yield and aspect-ratio controllable of Au BPs are the two key factors in obtaining high performance. Recently, high-yield Au BPs can be obtained by using the thermal treatment Au seeds due to drastic improvement penta-twinned nanoparticles and the aspect ratios of Au BPs could be readily tuned by simply varying the thermal treatment Au seed concentration. However, it is few research focuses on precisely tuning the reducing agent ability to control Au BPs size. It is well known that the reduced ability of polyol compounds has internal relation with the pH. In this work, we started with the commonly used reducing agent in the literature, that's ascorbic acid, by controlling pH below 7 to regulate the reaction rate and obtained Au BPs with average aspect ratios ranging from $\sim 1.69 \pm 0.14$ to $\sim 3.01 \pm 0.19$. Compared to ascorbic acid, the reduced ability of other polyol compounds, such as phenol, resorcinol or hydroquinone, are weaker. And they are not active enough to reduce Au ions to form BPs with seeds at the natural pH of the growth solution. To boost these hydroxybenzenes, higher pH is required to enhance their reactivity by adding base. Thus, we choose phenol as the reducing agent. We also demonstrated that the phenol's reactivity can be tunability by introducing base. The average length and width of Au BPs were from 22.1 ± 2.0 to 80.3 ± 2.7 nm and from 17.0 ± 1.5 to 25.4 ± 1.9 nm, respectively. The corresponding aspect ratios were from 1.30 ± 0.08 to 3.17 ± 0.22. In conclusion, this work demonstrated the pH can regulate the Au BPs size and it may be developed for the synthesis other noble metal nanostructures.
Circulary polarized light-driven assembly of gold nanostructures and their chirality measure

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Examples of converting spin angular momenta of circularly polarized photons into structural changes in matter are rare and known to display a low enantiomeric excess (ee). Synthesis of metallic NPs with chiral structures is one of the most intriguing study in field of nanotechnology due to its surprisingly strong optical activities in the metal-based electronic transitions in the visible region. Here, we demonstrate that illumination of Au precursors in the presence of citric acid with right- (left-) handed circularly polarized light (CPL) induces the formation of chiral Au nanostructures. Despite seemingly irregular shape of the particles, the resulted colloids showed distinctive mirror-imaged opposite circular dichroism (CD) bands according to the handedness of illuminated CPL. Circular dichroic response and geometric chirality from these seemingly achiral structures were successfully demonstrated and quantified by implementing three-dimensional (3D) electron tomography (e-tomo) into computational model. The ability of Au nanostructures to retain the polarization information of incident photons can be applicable to light-absorbing materials, thus to create a variety of chiral nanomaterials. Similar examination of seemingly irregular NP through suggested chirality measure can also elucidate previously puzzling optical response from unclear geometric asymmetry of nanomaterials.

Investigating the physical presence of vitamin E in lipid membranes

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Since its discovery over 90 years ago, the biological significance of vitamin E (tocopherol) has been surrounded by controversy. Putatively referenced as a potent fat-soluble antioxidant, α-tocopherol has also been linked to a diverse range of cellular processes including signalling, apoptosis, protein activity, and gene regulation, along with disease states such as infertility and neuromuscular dysfunction, though molecular mechanisms for the latter remain elusive. Considering the lack of conclusive investigations, the absence of a clear antioxidant health benefit from supplementation, and its significantly low physiological concentrations, skepticism builds regarding the true biological function of vitamin E. Since it localizes in the membrane, our research looks to address the physical perturbations of the membrane induced by the presence
Previous experiments on model membranes have revealed that α-tocopherol favours localization in less ordered lipid environments, specifically those provided by oxygen-sensitive polyunsaturated fatty acids – an association that is almost innate for an effective antioxidant. Moreover, through neutron diffraction and small angle X-ray scattering, α-tocopherol has been found to position itself precisely in the membrane to host a dual-faceted antioxidant mechanism, while not significantly altering the structure of the membrane.

Current investigations employ small angle neutron scattering with contrast matching techniques to study the effect of various tocopherols on domain formation. Organization of lipids into domains is thought to be an integral aspect of membrane functionalization as proposed by the lipid raft hypothesis. Using model large unilamellar lipid vesicles capable of phase-separation, the effect of tocopherol on domain stability is studied in both monounsaturated and polyunsaturated systems. Preliminary results indicate that increasing tocopherol concentration correlates to both the reduction and destabilization of ordered domains. Alterations in the membranes physical properties endorses the significance of vitamin E in membrane systems by suggesting a potential biological role beyond that of solely an antioxidant.

COLL 765

Hybrid polymer/lipid vesicles made from amphiphilic block copolymer poly(dimethylsiloxane)-b-poly(ethylene oxide) as cell-membrane-mimic: Formation, structure, and membrane properties

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Hybrid vesicles resulting from the combined self-assembly of amphiphilic copolymers and phospholipids have attracted particular interest over the last years. Such assemblies may be viewed as advanced vesicular structures compared to their liposomes and polymersomes forerunners as the best from the two systems can be combined (chemical versatility and mechanical stability from polymeric membrane, bio-functionality and permeability from lipidic membrane) and can be used in many applications: nano-reactors for enzymatic reactions, artificial biomimetic cell membrane, etc. Previous works in our group have allowed determining key parameters for the formation of unilamellar hybrid vesicles from micrometric to nanometric sizes (phospholipids fluidity, hydrophobic length mismatch, phospholipids mass fraction, etc.). Triblock copolymer PEO-b-PDMS-b-PEO use until now have however shown some limitations: unexpected mechanical stability of the hybrid vesicles with lysis strains below those of liposomes. This may be due to the architecture of the copolymer which is at the origin of a mix of U-shape (hairpin) or extended chain conformations inside the
membrane. To insure a bilayer conformation, in analogy to phospholipid in liposomes, a series of diblock PDMS-\textit{b}-PEO has been synthesized. The obtained diblock copolymer can form very easily nanosized and microsized polymersomes with tunable membrane thickness and high mechanical stability. Finally, the mixing with phospholipid leads to large hybrid unilamellar vesicles (LHUVs) and giant hybrid unilamellar vesicles (GHUVs). We modulated the copolymer molar mass and the lipid fraction to tune both the membrane structuration (homogeneous membrane, phase separation, budding) and the membrane properties (mechanical strength, fluidity). Finally, we obtained vesicles with a high tunability of the membrane properties in order to overcome most of the present limitations in the field of liposomes/polymersomes.

A- Scheme of a hybrid polymer/lipid vesicle presenting different struturations
B- Scheme of different polymer chain conformations
C- Confocal fluorescence microspe image of giant hybrid vesicles (GHUVs) showing phase separation between lipid and copolymer

**COLL 766**

**Molecular thermodynamics of receptor competition for uptake by endocytosis**

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Internalization of receptors from the cell surface regulates diverse physiological processes from the rate of nutrient uptake to the timescale of signaling events.
Specifically, cells tune the number of receptors on their surfaces by balancing the rate of receptor delivery with the rate of receptor uptake by endocytosis. The established view is that internalization of receptors is individually controlled by specific biochemical binding interactions. However, work from several groups has suggested that the internalization machinery is saturable by high levels of receptor expression, an effect which has the potential to couple internalization of one receptor to internalization of other receptors present on the cell surface. Specifically, how might the uptake of an individual receptor be impacted by uptake of other receptors that compete with it for limited space within endocytic structures? Here we show that the expression of competing receptors substantially alters the uptake of a model receptor. In particular, endocytic uptake of the model receptor decreased as the number, size, and affinity of its competitors increased (A-C). These competitive effects were well described by an equilibrium thermodynamic model in which the entropic cost of confining receptors within endocytic vesicles was paid by the reduction in free energy associated receptors binding endocytic structures (D,E). This work creates a framework for predicting the impact of competition on receptor recycling by endocytosis. In particular, understanding the physiochemical mechanism behind this competition is critical for predicting receptor uptake in settings where endocytic machinery approaches saturation, as is frequently the case in cancerous cells, which overexpress multiple receptor species associated with tumor growth and metastasis.
Competing receptors reduce endocytic uptake of a model receptor with increasing affinity for coated pits.

**COLL 767**

**Compartments and crowding: Biophysical features of living cells**

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The interior of a living cell is packed with large macromolecules (e.g., nucleic acids, proteins, polysaccharides,), cytoskeletal filaments, and dissolved salts. In aqueous solutions, these components often do not mix ideally. Differences in their solvation, inter- and intramolecular interactions, and electrostatics render the aqueous cytosolic space inhomogeneous producing a patchwork of co-existing fluids. This microcompartmentalization is thought to arise through thermodynamic liquid-liquid phase separation at equilibrium. But how is it affected by the macromolecular crowding in the cytoplasmic space? Do non-equilibrium processes, such as of molecular additions and removals present in living cells, alter these equilibrium tendencies? How this dynamic micro-compartmentation affects membrane shapes and molecular organization?

Building on the experimental model system, developed previously by Keating (PNAS, 2005), Dimova, and Lipowsky (Soft Matter, 2012), we reconstitute minimal crowding and conditions for dynamic microcompartmentation inside cell-sized giant vesicles. Specifically, we encapsulate a uniform aqueous phase mixture of two water soluble polymers (namely, dextran and poly(ethylene)glycol), which when subject to osmotic deflation, assumes relative concentrations that produce aqueous two-phase separation (ATPS) in real-time. We find that the onset of vesicular micro-compartmentation in the encapsulated aqueous phase experiences a competition with preferential wetting of one of the forming phases by the bounding membrane arresting phase coarsening. Interestingly, this also drives an active membrane remodeling inducing vesicle morphogenesis. Unlike equilibrium configurations, we find that multiple buds of essentially uniform size decorate the membrane boundary reflecting a competition between phase coarsening dynamics during the spinodal decomposition of the ATPS and preferential wetting of the membrane surface by the dextran-rich phase. Our results suggest the stabilization of a rich variety of membrane morphologies through kinetically determined membrane deformation processes, far exceeding the narrow range of shapes obtained under thermodynamic equilibrium.

**COLL 768**

**Activation of the EphA2 receptor tyrosine kinase by a conditional transmembrane peptide**

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We have transformed the isolated transmembrane sequence of EphA2 into a conditional, pH-controlled, TM domain. The resulting peptide, TYPE7, is highly soluble, interacts with the surface of lipid membranes, and upon acidification inserts and folds
into a TM helix. The receptor tyrosine kinase EphA2 plays an important role in cell-cell contacts, cell migration, and cancer metastasis. Importantly, when TYPE7 inserts into membranes, it binds to endogenous EphA2, as shown in liposome and cellular experiments. This new interaction specifically results in the phosphorylation of the key catalytic residue Tyr772, present at the activation loop of the intracellular kinase domain. Binding of TYPE7 to EphA2 also causes a downstream signaling change, in the form of de-phosphorylation of Akt, a central regulator of cell migration. In fact, TYPE7 inhibits cell migration as efficiently as an EphA2 ligand in several cell lines. We characterized that the mechanism TYPE7 uses to activate EphA2 involves promotion of EphA2 self-assembly into oligomers. Our work highlights the use of biophysical approaches to develop a new method to create synthetic ligands for receptor tyrosine kinases. These new conditional transmembrane ligands will not only provide new mechanistic information on the target receptor, but also serve as potential therapeutic molecules.

**COLL 769**

**Direct cytosolic delivery of macromolecules via connectosomes**

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Inefficient transport across the plasma membrane has greatly hindered the clinical success of siRNAs and other hydrophilic macromolecules. To traverse this selective barrier, existing technologies employ cationic lipid carriers. These carriers enter cells through endocytosis where they release siRNAs into the cytoplasm by bursting endosomal membranes. This inefficient and poorly controlled process contributes strongly to the systemic cytotoxicity of existing siRNA therapeutics. Nature, however, has provided an elegant route for direct delivery of siRNAs to the cytoplasm – the gap junction network. This network of transmembrane channels physically connects the cytoplasm of adjacent cells, and thereby provides a direct passageway into the cytoplasm. To harness the potential of this machinery for molecular delivery, here we demonstrate the transport and delivery of macromolecules using Connectosomes, cell-derived plasma membrane vesicles that contain high concentrations of gap junction proteins (A). Specifically, our results illustrate gap junction-mediated loading of both siRNAs and 10 kilodalton dextran into Connectosomes (B) and the subsequent transfer of these macromolecules into the cellular cytoplasm. Using Connectosomes, we achieve potent silencing of green fluorescent protein expression (C). Further, the delivery efficiency of dextran increases by about 40-fold in comparison to the passive cellular uptake of free dextran in solution (D). These results demonstrate the potential of Connectosomes to effectively address the long-standing challenge of crossing the plasma membrane barrier. Moving forward, this increased delivery efficiency will create new opportunities for delivering siRNAs as well as other classes of therapeutic biomolecules, such as short signaling peptides.
A) Gap-junction mediated siRNA delivery. B) siRNA loading into Connectosomes. C, D) Efficient delivery of siRNAs C) and dextran D) into receiving cells.

**COLL 770**

Supported lipid bilayers of *Escherichia coli* extracted lipids and their substrate and calcium dependence

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Artificial lipid membrane is widely used for studying cell membrane property, drug development, and biosensor. Supported lipid bilayers (SLBs) are a kind of artificial lipid membrane situated at solid-liquid interface. SLBs have been used to investigate the fundamental physicochemical properties and molecular distribution of lipid bilayers. As a bacterial model cell system, a reconstituted *Escherichia coli* (E. coli) cell membrane has been studied. Understanding the bacterial membrane system supports to reveal the mechanism of molecular recognition and material transportation during bacterial infection for medical technology. The *E. coli* lipid extract contains three main phospholipids, phosphatidylethanolamine (PE), phosphatidylglycerol (PG) and cardiolipin (CA). In this study, we formed SLBs of the *E. coli* extracted lipid on mica and thermally oxidized SiO₂/Si substrates, and investigated them with atomic force microscopy and fluorescence-microscope-based methods. We found substrate-
dependent SLB formation, and two- and three-dimensional morphologies depending on Ca²⁺ concentration. We also formed SLBs of *E. coli* extracted PE, PG and CA. These three major phospholipids showed various SLB formation and morphologies depending on the substrates and Ca²⁺ concentration.

**COLL 771**

**Lipids alter rhodopsin function via solvent-like and ligand-like interactions**

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Rhodopsin is a highly efficient photoreceptor that, when excited by light, can activate the signaling pathway that leads to scotopic vision in mammals. This activation process requires the transduction of an external light stimulus across the membrane in which the protein is embedded via conformational changes. Experimental evidence has shown that rhodopsin's activity and structural stability is sensitive to the composition of its lipidic environment. However, the molecular mechanisms underlying this fine-tuned modulation are not fully understood. There are two hypotheses—often presented as mutually exclusive—that have been proposed to explain the nature of lipid effects on rhodopsin: 1) lipid modulation occurs via solvent-like interactions, where lipid composition controls membrane properties like hydrophobic thickness and acyl chain packing, which in turn modulate the protein's conformational equilibrium; or 2) lipid modulation occurs via ligand-like protein-lipid interactions, with specific hot spots and long-lived binding events. Here, we analyze an ensemble of microsecond-scale all-atom molecular dynamics simulations of rhodopsin in five different protein states to investigate the molecular details of lipid modulation in this receptor. Our simulations suggest that both solvent-like and ligand-like properties of lipids can influence rhodopsin's structure and function. By comparing multiple protein states along the protein's photocycle, we show that a local reordering effect takes place in the membrane upon receptor activation (a solvent-like effect). Likewise, we find that lipids can behave like weak ligands, preferentially binding to the receptor in inactive-like protein conformations and inducing subtle but significant structural changes (a ligand-like effect).

**COLL 772**

**Cholestrol-induced microdomains formation in completely miscible lipid bilayers which promotes the fusion of proteoliposome**

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There is growing concern on fusion efficiency of proteoliposome (PL) as it is vital for the reconstitution of ion channels into artificial lipid bilayer. Recently, we discovered the formation of microdomains on a ternary lipid bilayer consisting of egg-derived phosphatidylcholine (PC), phosphatidylethanolamine (PE) and cholesterol (Chol) which function as specific fusion site for PL.

In general, phase separation occurs in ternary lipid bilayers containing Chol and partially miscible lipids such as dipalmitoyl and dioleoyl PCs. However, in this study we used egg-derived PC and PE which are both in liquid crystalline phase and are both completely miscible without Chol. Formation of domains in completely miscible lipid bilayers after additional of Chol is an exceptional phenomenon. For that, we investigated the composition of this unique microdomain formation. Based on our discovery on microdomains, we proposed that increment in the area fraction of microdomains by manipulating the composition and concentration of lipid bilayers will ultimately lead to increment in fusion efficiency of PL. In this study, we investigated the effects of PE concentration ($C_{PE}$) and types of PE on microdomains formation as PE assists the fusion of two bilayer membranes due to their intrinsic negative curvature.

We prepared PC+PE+Chol-SLBs using egg-derived and synthetic PEs at $67-C_{PE}:33:0.26$ (molar ratio). The increment in $C_{PE}$ facilitated the formation of planar SLBs from vesicles and increased the area fraction of microdomains ($\theta$). Microdomains were in liquid-disordered-like state and PE-rich. PE with polyunsaturated chains such as the docosahexaenoyl group was the key factor of the microdomain formation. The results showed that PE with docosahexaenoyl group had the largest $\theta$ among egg-derived PE and dioleoyl-PE. The fusion efficiency of PL increased in the PC+PE+Chol-SLB containing docosahexaenoyl-PE.
The area fraction of microdomains in PC+PE+Chol-SLBs

COLL 773

Investigating interactions and stability of bacteriorhodopsin upon entrapment in sol-gel derived porous materials

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Bacteriorhodopsin (BR), a visible-light absorbing membrane protein, was encapsulated in sol-gel derived porous silica and titanium dioxide (titania) monoliths in its native purple membrane form. Sol-gel synthesis procedure was optimized to minimize the amount of alcohol in the pores to avoid denaturation of the entrapped protein. Fluorescence spectroscopy was used to investigate the effect of pH on thermal
denaturation of bacteriorhodopsin in silica. The amount of buffer added during the gelation of silica affected the stability of the protein at elevated temperatures. Intrinsic tryptophan fluorescence emission and anisotropy measurements showed that the protein was more stable at higher temperatures when pH was close to neutral. Solvent accessibility determined using acrylamide quenching of tryptophan residues indicated similar environment for the protein before and after entrapment. The absorbance spectrum of BR entrapped in both silica and titania gels demonstrated retention of the protein tertiary structure. It was also shown that the protein could undergo conformational changes from its dark to light adapted states after entrapment in both matrices. Förster resonance energy transfer between tryptophan residues and titania sol nanoparticles suggested there is less than 10 nm separation between bacteriorhodopsin and titania surface. These results lay the groundwork for development of functional biocompatible porous materials using membrane protein encapsulation.

COLL 774

Sizes and yields of giant unilamellar vesicles using cellulose paper and cotton fabric

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Lamellar phospholipid stacks on cellulose paper vesiculate to form cell-like giant unilamellar vesicles (GUVs) in aqueous solutions. The sizes and yields of the GUVs that result and their relationship to the properties of the cellulose fibers are unknown. Here we compare the characteristics of GUVs produced on four different cellulose substrates, three disordered porous media consisting of randomly entangled cellulose fibers (high purity cellulose filter papers of different effective porosities) and an ordered network of weaved cellulose fibers (cotton fabric). Large numbers of GUVs formed on all four substrates. Our result demonstrates for the first time that GUVs form on cotton fabric. Despite the differences in the configuration of the cellulose fibers, all four substrates yielded populations of GUVs with similar size distributions with a single well-defined peak and a right-tail. Cotton fabric produced the highest yield of GUVs with the lowest sample-to-sample variation. Moreover, cotton fabric is reusable, thus providing an environmentally-friendly route to scaling up production of GUVs.

COLL 775

Multi-coordinating polymer ligand for the functionalization of semiconductor, metal, and metal-oxide nanoparticles

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It has been shown that colloidal nanocrystals made of semiconductor, metal and metal-oxide cores have a great potential for use in several biological applications. These materials are often grown in organic solutions; they are hydrophobic which limits their biocompatibility. Different surface functionalization strategies have been explored to render them hydrophilic. One effective route relies on cap exchange with coordinating ligands. We hereby report the design and optimization of a set of phosphonate-based polymers as versatile multi-coordinating ligands applicable to semiconductor, metal, and metal oxide nanocrystals. Ligand synthesis relies on the nucleophilic addition reaction between poly(isobutylene-alt-maleic anhydride) and amine-modified phosphonates combined polyethylene glycol and reactive moieties. The synthetic route is effective and allows control over the ligand stoichiometry. Nanoparticles capped with such ligands are sterically stabilized in a broad range of biological conditions and furthermore reactive. Additionally, the polymer coating is amenable to the introduction of additional functionalities such as $^{19}$F labels. We will discuss the preparation of a set of multimodal platforms, with controlled solubility, and their use in few sensing as well as tissue and cell imaging applications.

**COLL 776**

Interchange of L-, Z-, and bound-ion-pair X-type ligation on cadmium selenide quantum belts

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Wurtzite CdSe quantum belts having Z-type ligation, such as \{CdSe[Cd(oleate)$_2$]$_{0.19}$\} QBs, undergo facile ligation exchange with AX salts (A = R$_4$N, Na; X = OH, Cl, Br, NO$_3$, OBz, OAc) to afford quantum belts having bound-ion-pair X-type ligation and empirical formulas CdSe[X]$_x$[A]$_x$. Exchange to AX ligation is accompanied by shifts of the quantum-belt absorption spectra by as large as 340 meV (for X = OH) relative to the spectrum of L-type \{CdSe[n-octylamine]$_{0.53}$\} QBs. The AX ligation appears to consist of two populations, one for which the AX ligands are persistently bound, and another for which the AX ligands are readily removed by washing. These generate two ligation stoichiometries referred to as depleted and saturated ligation, respectively. The empirical formulas for depleted ligation are in the approximate range of CdSe[X]$_{0.1-0.3}$[A]$_{0.1-0.3}$, whereas those for saturated ligation are in the approximate range of CdSe[X]$_{0.4-0.8}$[A]$_{0.4-0.8}$. These ranges are consistent with approximately one and two X- ligands per three-coordinate surface Cd atom, respectively. AX ligation is readily exchanged to either L-type primary amine or Z-type Cd(oleate)$_2$ ligation. However, AX salts do not displace L-type primary amine ligation under the conditions studied. All ligation exchanges are rapid and complete at room temperature, and with the exception of L-type to bound-ion-pair X-type ligation, fully reversible.
Ligand-capped colloidal metal nanoparticles are promising materials as selective catalysts for organic reactions. Its large surface area to volume ratio allows for high catalytic activity, while their ligands dictate the immediate surrounding environment at the catalytic surface site. Our group previously reported that the thiosulfate protocol using sodium S-alkylthiosulfates instead of alkanethiols generate catalytically active Pd nanoparticles (PdNP) capped with lower density of alkanethiolate ligands. In this method, however, the nanoparticle core size is established during the ligand passivation of the growing nanoparticles. The average core size of nanoparticles, therefore, depends on the amount of ligand precursors added, resulting in the formation of nanoparticles with lower surface ligand density but with increased core size and vice versa. Herein, we report a modified synthetic method in which the core size of nanoparticles is determined independent of ligand concentration, allowing the formation of PdNPs with similar core size, yet with different surface ligand density. Briefly, the core size of PdNP is established during the temporary passivation of growing nanoparticles by borohydride and tetraoctylammonium bromide (TOAB), letting nucleation to reach completion. Various molar equivalents of alkyl thiosulfate are then added, prompting the replacement of borohydride and TOAB and the formation of PdNP with various surface ligand density. The direct comparison of the catalytic activity and selectivity of these PdNPs yields systematic understanding on the isolated effects of surface ligand density from other parameters such as core size and shape. The surface crowding and poisoning induced by alkanethiolate ligands clearly have strong influences on the selectivity between hydrogenation and isomerization of terminal alkenes. PdNPs with lower surface ligand density, which show an enhanced catalytic activity, demonstrate a decreased selectivity for isomerization possibly due to the presence of some active sites preferring hydrogenation products formed via the di-σ-bonded Pd-alkyl intermediate. This presentation also reports the synthesis and catalysis of binary ligand-capped PdNPs prepared with varying ratios of two dissimilar ligands but with similar core sizes. The influence of surface composition and morphology (e.g. phase-separated or random organization) on the catalytic activity and selectivity of binary ligand-capped PdNPs is investigated.

Molecular dynamics simulations of metastable peptide crystals: A cross beta transformation and selective adsorption of charged gold nanoparticles
Molecular dynamics simulations are used: 1) to examine the experimentally observed conversion of metastable cross alpha helical peptide crystals into thermodynamically stable cross beta-like fibrils and 2) to explain the selective adsorption of charged nanoparticles on these fibrils. First, the relative stability of peptide crystals was studied by simulating their different facets in a physiological solution. RMSDs of individual peptides at different facets were evaluated with respect to their initial configurations to examine their stability. The conformations of individual peptides in a physiological solution were also evaluated to examine their native stability at different temperatures and in the presence of electric fields. Next, ligated (charged) gold nanoparticles were simulated in the presence of cross beta-like fibrils (crystals) in the presence of 10 mM phosphate buffer at pH 7.4. The simulations have revealed a built-in electric field generated by the cross beta-like crystal, due its asymmetric structure. This electric field has directed the adsorption of the gold nanoparticle on the crystal surface, in agreement with the experimental observations.

**COLL 779**

**Ligand exchange on ternary sodium bismuth dichalcogenide using multidentate ligands**

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Solution grown colloidal semiconductor nanocrystals are stabilized by ligands that influence their stability, electronic, and optical properties. In contrast to unary and binary semiconductors, the surface chemistry and ligand exchange on various functional group in complex ternary and quaternary materials is little explored. Here, we synthesized biocompatible rock salt ternary NaBiS$_2$ nanocrystals through soft chemistry techniques that display size tunability (2-28 nm). We report a facile biphasic ligand exchange procedure that utilizes monodentate (iodine) and multidentate (thiol) ligands. This procedure efficiently displaces native carboxylate, amine, and thioamides that chelate to the surface of NaBiS$_2$ producing polar, water-soluble nanocrystals. We demonstrate that these thiol capped ligands can be functionalized with long, biocompatible polymers that further improve nanocrystal stability. Ligand exchange and nanocrystal stability were investigated by IR, MS, UV-Vis, TGA/DSC, and XRD. We anticipate that these finding will shed light on ligand exchange in other ternary and quaternary materials.

**COLL 780**

**Ligand design for direct optical (254nm, 365nm and 405 nm) and e-beam lithography of functional all-inorganic nanomaterials**
Direct optical lithography of functional inorganic nanomaterials (DOLFIN) has been introduced as a unique, photoresist-free method to pattern inorganic nanocrystals (NCs) with deep UV (DUV, 254 nm) exposure. Here, we design a series of novel ligands for NCs that can be directly patterned not only with DUV, but also with near UV light (i-line, 365 nm), and even visible light (h-line, 405 nm) using environmentally benign and industrially accepted solvents. By designing the photochemically active NC surface ligands, we show that DOLFIN can be easily carried out with a dosage of 30 mJ/cm². In addition, we introduce a general approach for direct electron-beam lithography (EBL) of functional inorganic nanomaterials (DELFIN) without using photopolymers or other resists. By utilizing the advantages of EBL, all-inorganic NCs patterns with features down to 30 nm can be obtained. We also demonstrate that the optical and electrical properties of patterned inorganic materials are well preserved. The new ligand chemistries and patterning techniques provide a more versatile platform for lithography and additive nanomanufacturing, complementing the existing toolbox for thin film device fabrication.

**COLL 781**

Photoligation with lipoic acid ligands is an effective strategy for preparing biocompatible gold colloids

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In recent years, gold nanocolloids (e.g., nanoparticles, nanorods, and nanostars) have generated much interest for use in biomedical research, due to their unique plasmonic features and reported low cytotoxicity. Synthetic methodologies such as hot-injection of gold precursors in oleylamine solution and hexadecyltrimethylammonium bromide-stabilized seeded growth were developed to prepare gold nanostructures with various sizes and shapes. Integration of the as-synthesized nanomaterials into biology requires access to hydrophilic nanocrystals with guaranteed long-term colloidal stability and biocompatibility. We hereby introduce a photo-promoted ligand exchange of gold colloids with a series of lipoic acid (LA)-based ligands (including monomeric and polymeric ligands), which can be rapidly implemented (with times required of ~20 - 30 min.), while consuming substantially smaller amounts of ligands, compared to “conventional” phase transfer strategies. We applied this procedure to several gold colloids with great success. The strategy also allows the introduction of various reactive groups onto the nanocrystal surfaces. For instance, ligation with polymeric ligands made of LA and PEG-modified poly(isobutylene-alt-maleic anhydride), can easily provide nanocolloids surface functionalized with controllable numbers of carboxylic acids, amines or azides.
The final nanomaterials have been characterized using dynamic light scattering, transmission electron microscopy, pH-stability tests, and further tested in sensor design.

**COLL 782**

**Basal plane functionalization of group V and VI layered transition metal dichalcogenides**

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Utilization of Group V and VI 2H-MX₂ Transition Metal Dichalcogenides (M = Mo, W; Nb; X = S, Se Te) in chemical sensors, thermal-optical coatings and structural nanocomposites require direct chemical modification of the chalcogenide basal surface. Defect termination with elemental chalcogenide or organic ligands with terminal chalcogenides are routine, however provide only limited control of functionalization density. Current hybridization strategies rely on extreme reduction processes to drive a transformation from the inert 2H to the reactive 1T phase. Conversion back to the 2H phase though is incomplete, resulting in heterogeneous materials. Here in, we demonstrate an alternative method for direct hybridization of Group VI 2H-MX₂ TMDs via alkyl organometallic reagents and Group V 2H-MX₂ with Lewis acid-base donor-acceptor chemistry. Using the recently development redox exfoliation method, single to few layer TMDs are stabilized in a range of polar organic solvents that are compatible with organometallic chemistries and various Lewis acid-base donor-acceptor moieties. X-ray Absorption Spectroscopy demonstrate strong chalcogen-ligand interaction while X-ray diffraction of assembled nanolaminates resolve an expanded interlayer gallery consistent with basally conjugated short-chain organics. The functionalized 2H-MX₂ TMDs can be transferred to non-polar solvents (THF, CHCl₃, CH₂Cl₂), and show enhanced stability from oxidation and degradation. Finally, the developed chemistries are tolerant to –ene and –yne pendant groups, facilitating post-functionalization modification via thiol-ene click chemistry or UV initiated -ene cross-linking allowing for the development of robust nanocomposites. Modulation of the optical and mechanical properties of NbS₂, NbSe₂ and MoS₂ is demonstrated.