COLL 1

Colloidal synthesis and characterization of size tunable luminescent Zn$_3$P$_2$ nanocrystals

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Among II-V compound semiconductors, Zn$_3$P$_2$ has proven to be an important candidate for photovoltaic applications due to its low toxicity and direct optical bandgap of 1.4–1.5 eV. Up until recently, reports of synthetic methods for Zn$_3$P$_2$ nanocrystals (NCs) have attracted more attention, but understanding of the tunability of their optical properties according to crystal size has remained a challenging job. Herein, we report the synthesis of size controlled tetragonal Zn$_3$P$_2$ NCs with tunable absorption and emission in the visible spectrum via hot injection of tris(trimethylsilyl)phosphine and diethylzinc in 1-hexadecylamine/1-octadecene at high temperature. The emission of the NCs was investigated as a function of growth time and temperature, exhibiting size-tunable maxima in the visible spectrum (469 – 545 nm). Solid State absorption spectra indicate considerable blue shifts in the absorption onsets (1.68 – 2.51 eV) with respect to the bulk (1.4–1.5 eV), consistent with quantum confinement effects. Surface studies of resultant NCs using FT-IR, TGA and XPS confirm the absence of metal and metal oxide, and also determine the passivation of amines via N–Zn and N–P bonds.

COLL 2

One-step seeded growth of quasi-spherical silver nanoparticles through a thermal process using hydroquinone as a selective reductant
Silver nanoparticles (AgNPs) have been the object of intensive investigations due to their unique optical, electrical and bio-active properties. Since their above properties are highly sensitive to size and shape, numerous efforts have been devoted to controllable synthesis of AgNPs. Among the various shapes, such as cubes and rods, prisms and branches, spherical NPs play a unique role in fundamental research because it is the only type for which the classical Mie’s theory provides an analytical solution of Maxwell equations. Compared with the production of AgNPs in organic media, aqueous syntheses of spherical AgNPs still remain significant challenges due to the process of nucleation and growth is difficult to separate. This study demonstrates a robust method for size-controllable synthesis of quasi-spherical AgNPs by a seeding-growth process using hydroquinone as a selective reductant in a aqueous solution. In the presented method, citrate-capped AgNPs with tunable sizes ranging from 15 nm to larger than 100 nm were achieved in a one-step growth process by varying the amount of qualified spherical 4 nm AgNPs as starter seeds. An important finding is that hydroquinone remains the selective reductive ability even at a boiling condition, enable the production of thermodynamic-favored spherical NPs. On the contrary, conducting the reaction at routine room temperature in the presence of hydroquinone without the change of other parameters, most of the resultant particles were kinetic-favored prisms. We expect this contribution may also help to improve the quality of other noble metal NPs when employing the seeded growth processes.

COLL 3

Palladium nanoparticle seed mediated growth of palladium nanoshell on silica core

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Palladium shell of ~11 to 15 nm thickness has been synthesized successfully by reduction of surface bound palladium ions onto ~200 nm diameter silica core. The method for generating such nanoshells is based on seed-mediated growth technique. Palladium ions from complex palladium salt are adsorbed onto aminosilane functionalized silica core and subsequently reduce to create in situ palladium nanoparticle seeds. These nanoparticle seeds act as the nucleation sites to promote further growth of final palladium overlayer. Palladium nanoparticle seeds generated onto the functionalized silica surface are ~3nm in diameter and are uniformly distributed throughout the core surface as observed by transmission electron microscopy (TEM). The thickness of the final palladium shell can easily be tailored by varying the concentration of the seeded core during the shell formation step. An increase concentration of seeded core leads to decrease in shell thickness. In addition, use of ascorbic acid generates uniform shell compare to formaldehyde as reducing agent. The formation of the palladium nanoshells is extensively monitored using ultraviolet-visible
spectroscopy and TEM, with zeta potential measurement to assess the surface charge of silica core and after surface functionalization. This present method reports the first time synthesis of palladium nanoshell from surface bound palladium nanoparticle seeds compare to all the earlier reports that use gold nanoparticle as seed to generate the final palladium shell.

**COLL 4**

**Generation of surface active species through hydrolytic conversion of organotrialkoxysilanes and their use in particle synthesis**

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Organotrialkoxysilanes are widely used as monomers for the synthesis of tailored nanoparticles, e.g. hollow/porous organosiloxane spheres and polymer-organosiloxane composite particles. When preparing such particles in an emulsion-based process, the presence of a surfactant is required. In 2007, Saccano et al. disclosed that (3-methacryloxypropyl)trimethoxysilane forms a surface active species under alkaline conditions.[1] When organotrialkoxysilanes are used both as precursor for a surface active species and as monomer for the particle synthesis, it is of vital importance to control the kinetics of formation of the surface active species and the polymerization kinetics. Here, we present an extensive study on the kinetics of formation of the surface active species, using phenyltrimethoxysilane as a model. Furthermore, we characterized the surface active species formed under alkaline conditions. Based on the information obtained from both studies, we were able to rationally develop synthesis routes for the preparation of hollow and porous phenylsiloxane spheres and polystyrene-phenylsiloxane composite particles. [2] (see figure 1) We demonstrate that the effect is not limited to phenyltrimethoxysilane, but applies to a wide variety of organotrialkoxysilanes, which paves the way to introduce functional groups in and on the particles, such as thiol groups and acrylic moieties, for further modification of the particles.


Multifunctional colloidal magnetic nanoparticles by surface initiated atom transfer radical polymerization

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Magnetic nanoparticles are of huge interest in various areas of science, e.g. chemistry, biology, bio-chemistry, medicine or sensor technology.¹ The requirements for particles are as multifaceted as the areas, in which they are applied. For chemical applications, the particles need to be rapidly separable, inert and stable against harsh environment (temperature, challenging pH-values, solvents).² In contrast to this, medical, biological or sensor applications usually insist on dispersion stability in aqueous solutions, compatibility with biological relevant media, high saturation magnetization and/or the possibility for further modification.³, ⁴

Most of the different requirements are achieved using carbon coated ferromagnetic nanoparticles in combination with a covalently attached and controlled surface modification. The graphene-like coating enables a chemically stable and inert platform for atom transfer radical polymerization (ATRP).⁵ Surface initiated ATRP (SI-ATRP: polymer-growth from the surface) is feasible with a plethora of different monomers (desired functionality) and the polymerization can be well controlled (layer thickness and block-co-polymerization).⁴-⁶

Charged monomers (e.g. 3-Sulfopropyl methacrylate potassium salt (SPM)) can lead to highly stable dispersions and the stability can be tuned by the number of repeating units.⁴,⁵ Using poly(ethylene glycol) methacrylate (PEGMA) as monomer the highly lipophilic graphene layers can be turned into a hydrophilic and antifouling surface. Most challenging modifications require amphiphilic properties (dispersion stability vs. fast separation or lipophilicity vs. hydrophilicity). Such requirements need a coating with smart polymers, which can change their properties upon external trigger (temperature, pH etc.). By using N-isopropylacrylamide (NIPAM) as building block, the particles can
reversibly change between hydrophilicity and hydrophobicity by temperature change. Here we show the promising potential of SI-ATRP on magnetic colloids to design a desired nanomaterial for various applications.


COLL 6

Toward an improved understanding of the synthesis of alkanethiolate-protected Pd and Pt nanoparticles

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The two-phase Brust-Schiffrin synthesis been widely employed as a reliable method for generating small nanoparticles (1-10 nm) of a variety of different metals, including Au, Ag, Cu, Ir, Pd, and Pt. The thiolate-protected metal nanoparticle products of these syntheses are typically highly stable, relatively monodisperse, and can be dried, stored indefinitely, and redispersed without significant change. A thorough mechanistic understanding of these relatively complex, three-step syntheses using Pd and Pt, however, is still lacking. Here, the results of several mechanistic studies into the two-phase Brust-Schiffrin synthesis of thiolate-protected Pd and Pt nanoparticles are presented. UV-visible absorption, infrared absorption, Raman scattering, $^1$H NMR, TGA, and TEM have been employed toward developing an inventory of the chemical species present, and the reactions/processes occurring, at each stage of these syntheses. It is expected that the insights provided here will significantly improve understanding of these complex syntheses, and offer greater control over their nanoparticle products.

COLL 7

Morphogenesis of shapes and porosity of mesoporous silica particles

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Mesoporous silica particles are of broad interest for many photonic applications, filtration, drug delivery, catalysis. Here we study the synthesis of mesoporous silica particles which have a peculiar multi-micron shape and long cylindrical pores of 4-5nm.
We observe a three-step mechanism of the shape formation (morphogenesis) of these particles. Nanoporous nanoparticles of 20 to 50 nm in size are formed in the first step. During the second step, those nanoparticles form large micron size aggregates. And finally, during the third step, those large aggregates re-shape them self into well-ordered micron size mesoporous silica particles. We demonstrate that a mathematical model describing free energy of the cylindrical pores predicts their self-sealed geometry. To demonstrate the self-sealing of the pores, we use a fluorescent cationic dye to observe its diffusion inside the particles. Self-sealing pores prevent dye molecules from defusing inside the particles. We indeed observed such phenomenon but only at the later stage of the particle synthesis. So we conclude that the long cylindrical pores inside the micron size mesoporous silica particles are formed by aligning of cylindrical pores of individual nanoparticles, and this alignment keeps forming within the large micron size aggregates by forming domains, which eventually reach the size of the entire particles. According to the model, it is accompanied by the decrease of free energy. Accelerating the rate of silica condensation may result in insufficient time needed to form the domain as large as the entire particles. This leads to the presence of a number of pores which are not self-sealed. Besides fundamental understanding of the mechanism of morphogenesis and pore formation, this finding may be used, for example, to make particles with desired release of various substances from semi-sealed cylindrical pores.

COLL 8

One-pot synthesis, anisotropic blue emission, and gas sensing behaviors of ZnO supercrystals with controlled structures

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A series of ZnO supercrystals including twin-spheres exposed in ±(001) facets, dumbbells and prisms can be synthesized on large scale with a one-pot approach based on reactions taking place in nanoreactors consisting of AOT surfactant and Zn2+ ions. It was found that AOT surfactant can dramatically affect the growth of ZnO supercrystals. A stepwise self-assembly growth mechanism is proposed to understand the formation of the unique structures of the ZnO supercrystals. In addition, our recent work concerned with carving the ZnO supercrystals to obtain hollow nanoarchitectures will be discussed also. A library of ZnO supercrystals with controlled structures can be established conveniently by tuning the reaction parameters including molar ratio of AOT to Zn2+ ion and reaction temperature. The ZnO twin-spheres exhibit anisotropic blue emission for their special surfaces covered in polar ±(001) facets. It was also found that the ZnO supercrystals show excellent gas sensing performances related to their surface structures.
Tragedy of TOPO-bound CdSe nanocrystals: Illustrative lessons in failed synthesis

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For years the field of metal chalcogenide nanoscience, in particular the chemistry of colloidal cadmium chalcogenide nanocrystals, relied on a simple model, where the solvent during nanocrystal synthesis remained as the ligand after nanocrystal isolation. This led to many reports and depictions of cadmium chalcogenide nanocrystals bound by tri-n-octylphosphine oxide (TOPO). Careful analytical work, however, discovered that acidic impurities in TOPO are actually responsible for nanocrystal growth, and lead to the discovery that cadmium alkylphosphonates are the primary ligand binding TOPO-derived cadmium chalcogenide nanocrystals. Through an introduction to the covalent bond classification system and its application to metal chalcogenide nanocrystals, this talk will describe attempts to synthesize the elusive TOPO-bound CdSe nanocrystal. The surface chemistry of CdSe nanocrystals will be detailed through three related studies focused on exchanging X-, L-, and Z-type ligands.

Single-micelle-templating synthesis of mesoporous silica and organosilica nanotubes

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Mesoporous silica and organosilica nanotubes were synthesized using Pluronic triblock copolymer surfactants in a single-micelle-templating process. The materials form at relatively low ratios of the framework precursor to the surfactant. The materials were characterized using nitrogen adsorption, small-angle X-ray scattering and transmission electron microscopy. The nanotubes had the inner diameter around 10-15 nm. While Pluronic F127 with large hydrophilic poly(ethylene oxide) (PEO) blocks is advantageous in the synthesis of silica nanotubes, the formation of organosilica nanotubes can be observed when Pluronic P123 with moderate size of the PEO blocks is used. Our work shows the challenges and opportunities in achieving the nanotube structures through the single-micelle-templating process.

Pseudomorphic transformation: Simultaneous functionalization of silica microspheres and synthesis of bimodal SBA-15/MCM-41 with bottleneck pores

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Following the pseudomorphic transformation pathway non-agglomerated amino-functionalized mesoporous silica microspheres are synthesized by a one-pot synthesis from a parent silica (pores >30 nm) material. Narrow pore size distributions in the range from 3 to 5 nm are obtained with alkyltrimethylammonium structure-directing agents (SDAs), the particle size distribution and spherical morphology of the parent silica are retained during the synthesis. The products contain accessible and uniformly distributed amino groups. The average pore size and the ratio of small uniform mesopores (<5 nm) to larger mesopores and macropores can be controlled by choosing the appropriate SDA and by adjusting the concentration of the amino-functionalized alkoxy silane precursor, leading to a variety of meso-macroporous hybrid materials. When starting with a mesoporous parent material, SBA-15, a bimodal pore system can be produced. The transformation yields particles with bottleneck pores which block probe molecules, PAMAM (G3) coupled with fluorescein, viewed by confocal laser scanning microscopy. Nitrogen sorption also indicates pore blocking by a forced closure of the desorption isotherm.
Condensation of nucleic acids by multivalent ions

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Highly charged nucleic acid (NA) molecules are expected to repel each other, yet can be condensed by certain multivalent ions into structured aggregates. Recent experiments demonstrated that subtle differences between nucleic acids can lead to very different condensation trends: double-stranded (ds) RNA helices resist condensation under conditions where short DNA duplexes condense readily. We combine experiment, theory, and atomistic simulations to propose a mechanism that connects the observed variations in condensation propensity of short NA duplexes with the spatial variation of counterion binding at the NA duplex surface. Specifically, condensation propensity is determined by the fraction of counterions bound to the external (outermost) surface of the double-helix. A simple model is developed that provides semi-quantitative agreement with experiment, including subtle sequence effects on condensation propensity. Latest developments and experimental verification of the model will also be discussed.
Different counterion binding modes in DNA and RNA

**COLL 13**

*Self-assembled gene carriers of DNA and graft copolymers*

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Nanoparticles formed through complexation of plasmid DNA and copolymers are promising gene-delivery vectors, offering a wide range of advantages over alternative delivery strategies. Notably, recent research has shown that the shape of these particles can be tuned, which makes it possible to gain understanding of their shape-dependent transfection properties. In earlier work, we achieved this shape tuning through the use of block copolymers and variation of solvent polarity. Now, by combining computer simulations and experiments, we demonstrate that the use of graft copolymers offers more parameters for the same degree of shape control without the need for organic solvents. Our simulations provide insight into the mechanism governing the shape variation as well as an effective model to guide further design of non-viral gene-delivery vectors. This study also demonstrates how significant new insights can be obtained via a systematic and close combination of experimental and computational work.
The design of nanoparticles that can induce specific structural transitions in nucleic acids is important for nanotechnology applications including gene delivery and nanoelectronics. It is known that in biological systems, the binding of cationic proteins, such as histones, induce structural changes in DNA or RNA, which can affect gene expression or cause the compaction of DNA into chromatin. The anionic backbone of the nucleic acids DNA and RNA allow for non-specific electrostatic interactions with cationic proteins, nanoparticles, or dendrimers. 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 nucleic acids upon binding. We vary the nanoparticle charge, ligand hydrophobicity, ligand length and gold core diameter to determine important factors governing NP/nucleic acid interactions.

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. Shape of the nanoparticle ligand corona as well as charge is shown to affect the wrapping of nucleic acids with the nanoparticle. RNA behaves differently with the nanoparticles, and does not bend for the same nanoparticle charge. Low salt concentrations and high nanoparticle charge cause greater disruptions the structure of both nucleic acids. We find that the roll parameter is the most important base-pair parameter for DNA bending. These results may be used to construct pseudo-phase
Using graphene-DNA interactions to control nanopore transport

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Among several challenges that impede application of solid-state nanopores for detection and recognition of biomolecules is the high speed of the nanopore transport and its stochastic nature. In this talk, I will describe our recent work on using DNA-graphene interactions to modulate the rate and character of DNA translocation. The results of our molecular dynamics simulations suggest that electric charge on graphene can enforce a DNA homopolymer to adopt strikingly different conformations depending on the nucleotide composition of the homopolymer. The conformational response is sensitive to even very subtle nucleotide modifications, such as DNA methylation. Furthermore, the charge of graphene is found to profoundly affect the rate of electrophoretic transport of a DNA strand through a nanopore in graphene: a positive charge accelerates the electrophoretic transport whereas a negative charge arrests the DNA motion. As a possible practical application of the effect, we demonstrate stop-and-go transport of DNA controlled by the charge of graphene.
COLL 16

Prediction of surface and pH-specific binding of peptides to metal and oxide nanoparticles

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The mechanism of specific peptide adsorption onto metallic and oxidic nanostructures has been elucidated in atomic resolution using novel force fields and surface models in comparison to measurements. As an example, variations in peptide adsorption on Pd and Pt nanoparticles depending on shape, size, and location of peptides on specific bounding facets are explained. Accurate computational predictions of reaction rates in C-C coupling reactions using particle models derived from HE-XRD and PDF data illustrate the utility of computational methods for the rational design of new catalysts. On oxidic nanoparticles such as silica and apatites, it is revealed how changes in pH lead to similarity scores of attracted peptides lower than 20%, supported by appropriate model surfaces and data from adsorption isotherms. The results demonstrate how new computational methods can support the design of nanoparticle carriers for drug release and the understanding of calcification mechanisms in the human body.

COLL 17

Simulation of surface-peptide interactions in an aqueous environment

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Surface adsorption properties of peptides are useful for the design of devices for applications in nanotechnology and bio-sensing. Accurate simulation of these properties requires parameterization and validation of force field models via the combined use of quantum mechanical studies and molecular dynamics simulations coupled with comparison with available relevant experimental data. Depending on the application, various surfaces may be considered such as silica, graphene and transition metal dichalcogenides (TMDs e.g. MoS$_2$). For each of these surfaces it is important to investigate critical properties such as the influence of surface defects, surface thickness, and the impact of the underlying substrate material. As an example of this, the surface interactions of small model peptides with a graphene surface were simulated, focusing on the binding enthalpy, free energy, and peptide morphology. The results of this study are useful for the development of residue-based coarse-grained models for rapid screening of designer peptide sequences obtained from peptide-panning (phage display) experiments.

**Effect of surface polarity on physisorption of biomolecules: Molecular modeling**

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Physisorption of biomolecules to surfaces plays a role in many applications including sensors, bio-adhesion, drug delivery, composites, and coatings. For example, it is known that structural changes of interfacial biomolecules are crucial for properties of sensing surfaces and thus device performance. However, the desired surface properties for optimal change in bio-molecular structure are difficult to predict. Computer simulations can provide detailed information on the interfacial dynamics and aggregation behavior between biomolecules and various surfaces. Using all-atoms MD simulations we investigated the interactions between DNA and silk with surfaces with variable polarity (graphene, graphene oxide and SiO$_2$ surfaces). Our simulation results showed that graphene denaturates biomolecules, whereas both single and double stranded DNA retains their base pairs and overall structure on polar surfaces. We found that pi-pi stacking is the key interactions for unfolding DNA on graphene but chemical groups on polar surface could prevent DNA from forming these interactions. For silk, its secondary structure was lost on both polar and non-polar surfaces but it was observed that graphene oxide with 20 % oxygen content can retain and recover ordered secondary structure better than more polar structure such as SiO$_2$ surface. Our results also found that combinations of electrostatic interactions, water bridging interactions and hydrogen bonds between silk and surface play a pivotal role in conformational changes and recovery motions of secondary structure of silk on surfaces. Overall, graphene has strong binding with biomolecules due to its propensity to form strong van
Designing sterically stable drug delivery vehicles via bio-inspired hybrid soft biomaterials

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Our objective is to investigate the design of sterically stabilized hybrid biomaterials through the self-assembly of a binary mixture composed of amphiphilic molecular species, such as PEGylated lipids, and phospholipids. The stable hybrid vesicles can be formed through the self-assembly of amphiphilic molecules in the presence of a suitable solvent [1]. We use a Molecular Dynamics-based mesoscopic simulation technique called Dissipative Particle Dynamics to simultaneously resolve the aggregation dynamics, structure and morphology of the hybrid aggregate [1]. In addition, we have extended our investigations to introduce Janus nanoparticles into the system to study the interactions of various sized nanoparticles with the hairy vesicles and the methods to harness the interactions between them by tuning the relative sizes of PEG chains and nanoparticles, the concentration of hairy lipids, and the relative interaction strength between lipid species and nanoparticles. The results of our investigations can be used for the design and prediction of novel hybrid soft materials for applications in the encapsulation and delivery of therapeutic agents.


Applications of model membrane architectures

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Supported lipid bilayers provide a reductionist system for studying many properties of cell membranes that are difficult to study in vivo. We are interested in membrane fusion, lateral organization among components in membranes and the elucidation of structure function relationships for integral membrane proteins such as ion channels. For studies of fusion we have developed architectures in which the membrane is held away from the solid support, either as a membrane patch or tethered vesicle, and assays have been developed to study vesicle or viral (in collaboration with Peter Kasson) fusion. For studies of membrane lateral organization we use imaging mass spectrometry where isotopic labels allow us to differentiate and quantify components with very high spatial
resolution. For studies of structure function relationships we have developed a new membrane interferometer design which should permit simultaneous interferometric measurements of integral membrane protein (or vesicle) conformation and electrical measurements.

COLL 21

Patterned polysaccharide networks on surfaces control the phase behavior of lipid membranes

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Hydrated networks of polysaccharides in the form of cell walls, periplasms, or gel-like matrices are ubiquitously present adjacent to cellular plasma membranes. Yet despite their abundance, many of the functions of polysaccharides in the extracellular milieu are unknown. Eukaryotic cells compartmentalize their membranes to carry out biological function. These domains are important for signal transduction, virus entry and budding, and for the development of degenerative diseases such as Alzheimer’s. The factors that govern the formation of these membrane domains are also incompletely understood. In this talk I will describe an experimental platform that consists of spatially patterned polysaccharide ligands on hydrophilic surfaces. Lipid membranes that are deposited onto these surfaces appear to interact directly with these polysaccharides. Because of this interaction, the spatial configuration of the polysaccharides controls the phase behavior of the membranes: inhomogeneous polysaccharide networks stabilize large lipid domains at the characteristic length scale of the network, while homogeneous polysaccharide networks suppress macroscopic lipid phase separation. Polysaccharide-patterned phase separation is thermally reversible—indicating that the effect is thermodynamic rather than kinetic—and preferential interactions of polysaccharide with ordered lipid phases seem to control patterning. The discovery that polysaccharide networks can control the length scale of domains in lipid membranes necessarily has implications for biological transport processes and potentially rationalizes some puzzling observations that differentiate the behavior of native cell membranes from model membranes. The exact nature of the interactions remains to be elucidated, and may be related to other observations of lipid domain patterning due to interactions of membranes with cytoskeleton proteins.

COLL 22

Covalent and sequence-specific DNA surface attachment chemistry for multiplexed single molecule measurements

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Single molecule studies of DNA have helped to unravel the complex biochemical processes that govern gene expression and regulation inside the cell. Although a number of methods exist for tethering DNA to solid substrates, they suffer from several drawbacks, including inefficient attachment of longer molecules, poorly characterized surface interactions, and significant heterogeneity at the nanometer scale.

To overcome the limitations of existing DNA surface attachment chemistry, we have developed a method to covalently tether DNA molecules to a switchable surface that enables high-resolution AFM without sacrificing the conformational freedom of the tethered molecules. The method uses the DNA base-pairing interaction to template a more stable covalent attachment through Cu(I)-catalyzed click chemistry. The tethered molecules can then be switched between a frozen state for AFM imaging, and a free state for biophysical measurements. The DNA-templated click reaction represents a clean, selective and efficient strategy for attaching long DNA molecules to a surface for single molecule measurements, such as force spectroscopy, optical tweezers and fluorescence. Additionally, it allows for parallel, sequence-specific attachment of different DNA molecules, which can potentially be used to create single-molecule nanoarrays via lithographic patterning. This approach can also be utilized to study the self-assembly of more complex biomolecular systems, where the DNA strands can serve as the seeds that nucleate the assembly process.

**Coll 23**

**Discovery of DNA codes for controlling the morphologies of nanomaterials and elucidation of its mechanisms for such a control**

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Discovery of the genetic code is one of the most important achievements in biology. Inspired by this pioneering work, we have reported discovery of DNA codes, i.e.,
different combination of DNA sequences, for fine control of the shape and morphology of nanomaterials, such as growth of gold nanoparticles of different shapes and surface properties from nanoprisms and silver nanoparticles of different shapes from silver nanocubes. Rules of shape control by difference DNAs and their combinations are summarized. While these new DNA codes can play an important role in rational design and synthesis of novel nanomaterials with predictive shape control and functional properties, such as imaging and catalytic activities, the molecular basis for such a DNA-encoded control and its mechanism for the growth is not understood.

To elucidate the mechanism of the DNA-encoded control of nanomaterial morphologies, we performed kinetic studies of gold nanoparticles growth from nanoprisms in the presence of different DNA sequences using several different methods, including UV-vis absorption spectroscopy, scanning electron microscopy, transmission electron microscopy and electrochemistry. Based on the results, a mechanism for the growth of nanoparticles is proposed with weak binding DNA allow growth of the edges and less on the surface while strong binding DNA blocks the growth at the edges and results in growth on the surface. Elucidation of the mechanism is important as it expands the boundaries of DNA mediated growth to other seed systems to code for formation of a variety of shapes in a more predictable manner. In addition, the mechanism may be applicable to DNA mediated growth of other metallic or combination of metal systems as long as the binding affinity is resolved.

References:

COLL 24

Interactions of bacterial lipopolysaccharides with gold nanorod surfaces investigated by plasmonic sensing

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The interactions between nanoparticles and cells are of great interest for applications such as nanomedicine and food safety. Here, we demonstrate that interactions between gold nanorods and bacterial surfaces are governed by the surface coating on the gold nanorods. Polymer-coated gold nanorod substrates are exposed to lipopolysaccharides from Pseudomonas aeruginosa, Salmonella enterica, and Escherichia coli, and attachment is monitored using localized surface plasmon resonance refractometric sensing. The number of lipopolysaccharide molecules attached per nanorod is
calculated from the shift in the plasmon maximum which results from the change in refractive index after analyte binding. We also examine plasmon shifts after lipopolysaccharide binding to colloidal gold nanorods. Both surface charge and surface chemistry are critical to gold nanorod-lipopolysaccharide interactions. Generally, we observe that more of the anionic lipopolysaccharides attach to the cationic gold nanorods than the neutral or anionic gold nanorods. Variation in lipopolysaccharide attachment is also observed between the bacterial species, demonstrating the potential complexity of bacteria-nanoparticle interactions.

**COLL 25**

**Polysaccharide and oligosaccharide effects on surfactant micelle structure and interactions in aqueous solution**

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Surfactants are well-known to self-assemble in aqueous solution and on surfaces to form a variety of nanostructures with varying and tunable shape, dimensions, mobility, local polarity, local concentration, and reactivity. The surfactant self-assembly in water can be modulated by added solvents and/or solutes, depending on the concentration and type of the additives and their corresponding interactions with the surfactant. In addition to fundamental considerations regarding such intermolecular and inter-assembly interactions, our research in surfactant-self-assembly modulation by additives is motivated also by practical applications where surfactants are typically one of several components in a formulation. In this presentation we review recently-published results from our research group on micelle structure and interactions in aqueous solutions of the common surfactant sodium dodecyl sulfate as affected by polar organic solvents, polymers (poly(ethylene oxide), cellulose ethers), or solutes (cyclodextrins). Quantitative information, obtained from analysis of small-angle neutron scattering data, on the location of the additives in the surfactant assembly reveals the interactions acting in such systems. Fundamental information on such interactions informs the formulation of multicomponent surfactant mixtures for a variety of practical applications.

**COLL 26**

**Rationalizing the self-assembly of poly-(3-hexylthiophene) using solubility and solvatochromic parameters**

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We have studied the assembly and crystallinity of poly(3-hexylthiophene) (P3HT) (M_n ≈ 28.2 kDa, regioregularity > 96%, PDI ≈ 1.3) in >100 binary solvent mixtures using UV-
Vis absorption spectroscopy, and it is clear that the identity of the poor solvent used to drive aggregation has a significant impact on the structural order and crystallinity of the P3HT aggregates in solution. Here we report our findings using Hansen solubility parameters (HSPs), specifically the solubility distance vector, Ra, and the Kamlet-Taft solvatochromic parameters of the solvent mixtures to better understand the dominant solvent forces driving the self-assembly of P3HT. We find that the directionality of the Ra vector provides a better measure of the crystallinity of the P3HT assemblies formed in the solvent mixtures than does the magnitude of the Ra vector. Our analysis of the Kamlet-Taft ($\alpha$, $\beta$, $\pi*$) and $E_T(30)$ solvatochromic parameters reveals that the $\beta$ parameter correlates best with the crystallinity of P3HT and that, in general, assemblies having higher structural order are formed in solvent mixtures with lower values of $\beta$.

**COLL 27**

**Self-assembly of nucleic acid amphiphiles**

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The density and arrangement of nucleic acids have been recognized as important for specific interaction with cellular surface receptors, enhancing nucleic acid binding affinity with complementary strands, and improving the stability against endonucleases. Self-assembly of nucleic acid amphiphiles is a facile approach to create micellar nanoparticles with a high-density nucleic acid corona. Here, we explore the use of polymers and hydrophobic drugs to access nucleic acid-based nanoparticles, and demonstrate that they are functional analogues of metal nanoparticle-based spherical nucleic acids.

**COLL 28**

**Surfactant self-assembly on single-walled carbon nanotubes (SWCNTs): Hydrodynamic properties**

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Single-walled carbon nanotubes (SWNCTs) are materials with structural, electronic and optical properties that make them attractive for a myriad of advanced technology applications. A long standing practical barrier to their use is that current means of synthesis produce mixtures that are heterogeneous with respect to all key defining metrics: chirality, diameter, length, electronic type and enantiomeric "twist." This multidimensional polydispersity problem hinders both the metrology of distinct chirality species and the implementation of those individual species in high tech applications. Advancement in separation techniques to sort tubes with increased speed and reliability has been an active area of research for many years. Many of these techniques rely on the use of surfactant-mediated dispersion. This prevents aggregation, enabling the
separation of individual tubes while preserving their native mechanical and electronic properties due to the non-covalent nature of the binding. The structure and properties of the SWCNT-surfactant complex are the governing factor in a number of established and emerging separation processes. Understanding how these properties are affected by specific SWCNT-surfactant combinations is essential to advancing separation science and protocols.

In this talk, we study the structure and properties of SWCNT-surfactant colloidal complexes using all-atom molecular dynamics for a number of bile salt and anionic surfactants commonly used in the experimental literature, with a focus on hydrodynamic properties. The hydrodynamic size relevant in many separation techniques depends not only on the size of the self-assembled complex, but also, to a great degree on the size of the hydration layer that forms around the colloidal structure, a mechanism which has not been fully understood for these materials. The simulation results suggest that the hydration shell in these systems is the result of a long range electrostatic coupling between the SWCNT-surfactant superstructure and the free ions in solution, with the subsequent hydration of the ions. Understanding this gives us the information necessary to estimate the mass of the SWCNT hydration layer per unit length, and therefore, the buoyant densities the tubes -- an experimentally relevant quantity. Comparison with available experimental data will be discussed.

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**COLL 29**

**New insights to distinct increase of spontaneous lipid transfer rate in bicelles**

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Bicelles composed of long- and short-chain phospholipids have been widely used as model biomembranes to study the physico-chemical behavior of biomolecules. The understanding of and investigation on spontaneous lipid transfer (or exchange) between bicelles via water phase, though important, remain mostly unexplored. Our recent result indicates that the discoidal morphology can enhance the spontaneous lipid transfer rate by two orders of magnitude compared to that of spherical unilamellar vesicles. In this report, lipid transfer rate among bicelles, consisting of zwitterionic long-chain dipalmitoyl phosphocholine (DPPC), charged long-chain dipalmitoyl phosphoglycerol (DPPG), and zwitterionic short-chain dihexanoylphosphocholine (DHPC) were investigated using
time-resolved differential scanning calorimetry (DSC) and small angle neutron scattering (SANS). It shows that the lipid transfer in bicelle is an enthalpically unfavorable yet entropically favorable process. As expected, increased DHPC composition results in a higher lipid transfer rates at the same order of magnitude (the maximal difference at the same temperature is around two folds from Q = 3.5 to Q = 2.5), presumably caused by the ‘defects’ (intermediate region) formed between crystalline-DPPC and L_α-DHPC domains. The same reason can also explain the accelerated lipid transfer in the presence of 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethylene glycol)]-2000] (DSPE-PEG2000). This study provides new insights into the exchange kinetics and stability of the biomimetic membranes composed of multiple components.

COLL 30

Incorporation behavior of lipophilic molecules into lipid bilayer membrane-based nanotubes

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Previously, we reported peculiar intercalation behavior of styrene molecules into single-walled bilayer nanotubes consisted of L-glutamic acid derivatives. In addition, we found that construction of polymer backbone between the monolayers improves morphological and microenvironmental stabilities.¹) This paper exhibits elucidation of intercalation behavior of various guest molecules to lipid bilayer membrane-based suprastructure consisted of glutamic acid derivatives. In this study, N-pyridiniopropanoyl-L-glutamide lipid with didodecyl groups (g_{12}-Py⁺) was selected for creating single-walled bilayer membrane nanostructures in aqueous system. g_{12}-Py⁺ was well dispersed in water by ultrasonication to produce clear to slightly turbid solutions. DSC measurements of the solution indicate distinct phase separation behavior. The addition of octadecanol brought about a lowering of peak top temperature at 43 °C (T_{c2}) by 10 °C. However, extremely large phase-transition enthalpy, larger than sum of T_{c1} and T_{c2}, were observed. These results indicate that octadecanol cocrystallized with g_{12}-Py⁺ within bilayer membranes. When pyrene was incorporated to g_{12}-Py⁺ aggregates, pyrene was well dispersed in aqueous solution, and positive Cotton effect has been observed at the specific absorption band of pyrene. In this paper, the mechanism on intercalation behavior of various gest molecules will be discussed.

[References]
Biosurfactants known as sophorolipids: Sophorolipids consist of a dimeric sophorose linked by a glycosidic bond to the penultimate hydroxyl group of an 18-carbon fatty acid. An attractive feature of sophorolipids is their production by fermentation at volumetric yields exceeding 300 g/L. To tailor the physical and biological properties of sophorolipids, our laboratory has developed a wide range of methods to modify sophorolipid structure. An overview of previous methods developed in our laboratory that allow selective modification at sophorose primary hydroxyl groups as well as esterification and amidation at the fatty acid carboxyl group will be given. This paper will
then focus on a new family of modified sophorolipids prepared by ring-opening cross metathesis (RO/CM). Reaction conditions and yields for RO/CM of LSL with \(n\)-alkyl acrylates, trans-3-hexene, 1-hexene and ethylene will be discussed. Ethanolysis of LSL RO/CM products generated a series of medium chain (C10-C14) SL-surfactants and fatty acid co-products. Values of surface tension reduction at the air-water interface vs. Log (C) for modified SLs were measured by the Wilhelmy plate method. Minimum surface tension values varied as a function of the hydrophobic character of modified SLs. The modified SL from RO/CM with 1-hexene (SL-14) gave the largest surface tension reduction and lowest CMC (to 34 mN/m and 0.15 mM, respectively) and showed a similar surface tension reduction behavior as \(n\)-Dodecyl-\(\beta\)-D-Maltoside (Mal-C12).

Increasing the number of carbons in the hydrophobic segment for the homologous series of \(n\)-alkyl sophorosides results in an almost linear decrease in log(CMC), with \(B = 0.18 \pm 0.03\). This number is smaller than that of other related surfactants such as alkyl-\(\beta\)-D-glycosides and alkyl-\(\beta\)-D-maltosides.

**COLL 32**

**Role of hydration in lecithin reverse micelle structure and gelation in cyclohexane: A molecular dynamics study**

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Reverse micelles formed via amphiphilic self-assembly in apolar media are highly dynamic and responsive aggregates with applications ranging from drug delivery and templation of nanomaterials to enhanced protein separation. In particular phospholipid reverse micelles have attracted much attention in solubilisation of hydrophilic molecules in organic solvents and because they can undergo a phase transition from a freely
running organosol state into a stiff, highly viscous organogel state. The gelation occurs due to the entanglement of reverse micelles as they elongate to wormlike reverse micelles (WRMs). This is induced by a polar gelation agent, e.g. water, but the exact mechanism remains unclear.

Here, we apply atomistic molecular dynamic simulations to characterize the governing factors of reverse micellar structure in a lecithin/water/cyclohexane system. In particular, we map the structure and dynamics of the enclosed water as a function of water-to-lipid ratio and micelle size, and find hydrogen bond bridges contribute less to the stability of the WRMs than what has been previously postulated for this system. Instead, at key role in the emergence of the lecithin WRMs in cyclohexane is the change of the lipid packing properties due to increased hydration. Finally, we discuss the findings in terms of experimental data and their extension to related organogel forming systems.


**COLL 33**

Shape persistence micelles having the same aggregation numbers with the Platonic solids

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A series of calix[4]arene-based lipids with alkyl chains of varying length were newly synthesized and found that some of them form spherical micelles with a defined aggregation number. These aggregation numbers are 6, 8, 12, and 20, interestingly coinciding the numbers of the Platonic solids. Synchrotron small-angle X-ray scattering (SAXS) patterns exhibited a sharp intensity minimum, indicating high symmetry and shape monodispersity. The size monodispersity of the micelles was confirmed with analytical ultracentrifugation and asymmetric field flow fractionation. The present results indicate that a suitable combination of tail length, head volume, and rigidity of the building block is necessary to attain the shape persistency. With a shape determination program of Dummy and molecular dynamics calculation, the micellar architecture was determined and an atomic scale model to reproduce SAXS profile was constructed.

We have a hypothesis that can rationalize why the aggregation numbers are taking such a discreet manner and chosen from the numbers of the Platonic solids; the aggregation number is determined by the J. J. Thomson’s theorem to determine the minimum electrostatic potential energy configuration of N electrons on the sphere.
surface that repel each other. We suppose this can be extended to the other spherical micelles when the aggregation numbers are small enough.

References
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COLL 34

Toward a better understanding of the self-assembly of poly(ethylene glycol)-functionalized hexaphenylbenzenes

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Control of self-assembly is of great importance in materials science. The aim of this work is to combine the dynamics of low-molecular weight amphiphiles with the stability of their high-molecular weight analogues in order to achieve a better understanding of the self-assembly of these molecules in solution and in bulk. In solution hexaphenylbenzene-polyethylene glycol (HPB-PEG) derivatives substituted with two and four PEG chains lead to fiber-like structures in aqueous solution. The hydrogel fiber formation is verified by special analytical methods of polarized and depolarized dynamic light scattering. The water content in the hydrogel fibers of HPB-PEG derivatives can be controlled by the substitution pattern of the amphiphile and by the length of the PEG chains. In bulk a series of propeller-shaped HPB substituted with one, two and four poly(ethylene glycol) chains as well as of an ortho-connected trimer of HPBs bearing
two PEG chains result in remarkable amphiphiles with supramolecular organization and suppressed dynamics. The emerging dynamic picture is that of practically frozen HPB cores that are surrounded by mobile PEG segments. The implications of this supramolecular organization stacked/immobile HPB cores and flexible/fast moving PEG segments with suppressed crystallinity to ion transport are discussed with respect to the conductivity measurements in amphiphiles doped with LiCF₃SO₃ salt at different [Ethylene glycol]:[Li⁺] ratios. Both in solution and in bulk, geometry, size and amphiphilicity of the molecules are decisive parameters for the formation of defined structures.

COLL 35

**Time and concentration dependent assembly of amyloid-like peptides into supramolecular nanostructures**

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Characterizations of amyloid like structures with converging approaches are important to understand their complex self-assembly mechanism and the causes of strong mechanical stability. In addition, predictable molecular organization, kinetics and mechanism of self-assembly processes are quite important in the context of designing novel supramolecular peptide nanostructures. Here, we analyzed *in situ* co-assembly kinetics of oppositely charged Amyloid Inspired Peptides (AlPs) to monitor time dependent nanofiber formation and sol-gel transition at different peptide concentration by SAXS and different techniques. The kinetics of AlPs nanostructure formation and detailed SAXS analysis of AlPs hydrogels was used to develop a structural model for co-assembled AlPs nanostructures. Increased knowledge on molecular kinetics of co-assembly of AlPs can facilitate the further modification of the designed structures, the development of therapeutic strategies for protein-folding disorders and advances in improved materials inspired from self-assembly of functional and pathological amyloids.

COLL 36

**Nanostructured thin polymer films with ordered fullerene-like nanoparticles arrays: Dissipative particle dynamics simulation**

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We present dissipative particle dynamics simulations of diblock copolymer brushes exposed to a selective solvent. Depending on the relative lengths of blocks, one obtains
spherical, cylindrical and lamellar microphase-separated nano-structures, respectively [1]. We demonstrate that fullerene-like nanoparticles being miscible with one of the polymer blocks, are able to self-assemble at the brush interface in a way that they follow the underlying microphase-separated brush structure [2]. Finally they form pattern of spherical aggregates or chains/stripes (Figure 1). Such a lateral organization of semiconducting nanoparticles on amphiphilic block copolymer matrices enables new hybrid photonics materials to be used in nanotechnology. First results of brush simulations with Janus-particles will be discussed as well.


Figure 1. Fullerene-like nanoparticles (red) on the microstructured surface of diblock copolymer brush. Anchored blocks are shown in dark-blue, free (sticky) block forming cylinders are shown in white.

COLL 37

Waterborne nanoceria/polymer nanocomposites: Enhanced properties through designed nanostructure

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In recent years nanoceria has attracted the interest of both industrial and scientific communities, because of its high reactivity and its oxygen buffering capacity. Moreover, hybrid ceria/polymer systems have shown strong UV absorbance, which are of interest for the development of protective coatings and photoactive layers in solar cells. In this work, a series of nanoceria-stabilised acrylic latex particles has been synthesized by Pickering emulsion polymerization in the absence of surfactant. All Pickering latices in
the series, ranging from 0 to 10 wt.% nanoceria, are film forming at room temperature and demonstrate ordered particle packing, as revealed by atomic force microscopy. Upon film formation, the nanoceria shells of the particles create a honey-comb structure extending throughout. The nanocomposites' UV-visible spectra show strong absorption in all regions of the UV, and the linear absorption coefficient for UVA and UVB wavelengths increases with increasing nanoceria content. The presence of ceria improves the thermal and mechanical stability of the nanocomposite, by increasing its softening point and raising its elastic modulus in the rubbery state, according to dynamic mechanical and thermal analysis. These observations are discussed in the context of the honeycomb architecture formed by the soft latex particles that are surrounded by hard inorganic particles, thus giving stability to the structure. The results presented here will be of great interest for the development of both high performance coatings and photoactive layers.

COLL 38

Investigating the efficiency of polymer dispersants on aggregation and adsorption of asphaltenes with different functional groups: A molecular dynamics simulation study

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Asphaltene precipitation causes significant problems in the recovery, transportation, treatment and refining of crude oils.* The aggregation and adsorption of asphaltenes can clog rock pores, alter their wettability, and inhibit flow through wellbores. For as much production loss that asphaltenes cause, this is still a relatively understudied topic. One solution that has been shown to work recently is the use of polymers as dispersants.** These compounds are proprietary and therefore the structures and mechanisms by which they operate are not known. The goal of this study is two-fold: 1) to determine the role of asphaltenes’ functional groups on their aggregation and adsorption behavior. 2) To understand the mechanisms of asphaltene dispersion using polymer dispersants. This study was conducted using Molecular Dynamics simulations; the asphaltenes and polymers were modeled using the CHARMM36 force field. The aggregations of asphaltenes with different functional groups were monitored in bulk solvents consisting of heptane and toluene. To study the adsorption behavior, we included a half-protonated alpha-quartz surface in the system. Subsequently, polymers with different polar heads and aliphatic tails were inserted into the simulations and their effects on asphaltene aggregation and adsorption were quantified. In addition, we outlined the mechanisms of asphaltene dispersion by identifying the molecular interactions between the asphaltenes and the polymers.


**COLL 39**

**Polymer brushes in restricted geometries**

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In this talk, I will present novel neutron reflectivity measurements of the structure of opposing polymer brushes as a function of confinement. I will compare these results to the structure of polymer brushes at a single interface as well as to high precision surface force apparatus measurements of the force required to compress and shear polymer brushes. Although good agreement can be obtained between physical experiments, simulations and theory under low to moderate grafting densities, ultra-high
density brushes offer new challenges and behavior that has not yet been fully addressed. Significantly, the experimental relaxation time of ultra-high density brushes formed by grafting from methods (ATRP) was found to be at least four orders of magnitude longer than that predicted by the Rouse model resulting in enormous hysteresis during compression. Yet, the shear performance of such brushes demonstrated excellent lubricity under compressions down to 35% solvent content. The findings are consistent with a reduction in solvent quality with compression leading to shrinkage or collapse of the brush under high compression (increasing polymer concentration), while still maintaining a region of well solvated chains in the overlap region between opposing brushes. Together, the results suggest that compression hysteresis is primarily due to intra-brush entanglements and collapse of the brush layer rather than inter-brush entanglements and brush–brush interpenetration. The importance of the ultra-high density, ultra-polydisperse brushes yielding favorable lubrication properties is that a highly durable lubricating layer can be formed from a “realistic” system versus the more ideal, monodisperse systems that have been primarily studied in the past.

Schematic geometry of the experimental system and measurements.

**COLL 40**

**Orientational assembly of anisotropic zirconium phosphate nanoplate in polyionic salt matrix**
The controlled assembly of anisotropic patchy colloids, such as nanoplates, requires themselves to be well-organized over large area at a certain orientation and packing density. Although progress has been achieved via Langmuir-Blodgett technique, electric field directed assembly, and flow-assisted alignment, it remains a challenge for the future to control the density and orientation, especially the anisotropic particle in the polymeric matrix. Here, we investigate the self-assembly of discotic α-zirconium phosphate (α-ZrP, Zr(HPO$_4$)$_2$·H$_2$O) nanoplates in the sodium poly(acrylic acid) solution. The phase behavior of charged nanoplate suspension displays a strong dependence on polyionic salt concentration, as the interplay between excluded volume and electrostatic interactions determines the phase transition of glasses, gels and liquid crystal states. The anisotropic rim-to-face interaction of nanoplate, which is driven by the ionic strength, can be finely tuned the orientation from ordered liquid crystal phase to the disordered gel phase as well as the matrix density from high density (~180wt%) to light gel (~0.3wt%). These α-ZrP discotic suspensions exhibit the stable nematic orientation at low polyionic salt concentration. When polyionic salt concentration increases, it follows with the phase transition from nematic phase to gel phase. In between the order-disorder (nematic to gel) transition, the orientation of nanoplate can be tuned easily by simply control the polyionic salt concentration. Moreover, intrinsic high anisotropic nanosheet enables the formation of highly ordered liquid crystal orientation at much reduced concentration and the polymeric matrix brings the extra-functionalities, such as gas barrier property. The study shows the nematic phase orientation remains in the sodium poly(acrylic acid) matrix where the polymeric matrix serves as the interlayer spacer. The thin film casted from light gel, however, presents the disordered rim-to-face network of nanoplates in the polymeric matrix. Due to the thermal sensitive rim-to-face interaction, the orientation of nanoplates in the polyion salt solution can also be modulated by heat, illustrating the reversible gel-liquid transition.

COLL 41

Surface forces associated with hierarchically structured layer-by-layer films of polymer brush grafted nanoparticles and star polymers

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Strong solvation of polymer brushes under good solvent conditions leads to long-range repulsive normal steric forces and low friction coefficients between opposing surfaces immersed in a liquid. Thus, the creation of polymer brushes is a frequently employed interfacial engineering strategy when minimal adhesion and/or low friction are desired. Several options exist to prepare a polymer brush on a surface, but most suffer from one
or more characteristics that limit their practical utility. For example, grafting of polymers to a surface is often unable to achieve high chain grafting densities that maximize steric forces and minimize brush interpenetration. Here we examine normal and frictional forces between surfaces modified by adsorption of polymer brush grafted nanoparticles (BGNPs) and star polymers that share the key structural feature of a large number of polymer chains emanating from a central core. The BGNPs or star polymers are synthesized with high grafting densities. Adsorption of these structures onto a macroscopic surface ideally could produce films that approximate essential features of a uniform polymer brush. We examine cationic poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA)-grafted silica nanoparticles and poly(ethylene oxide) (PEO) star polymers. These adsorb from water to negatively charged silica surfaces. Although it is possible to control the packing of PDMAEMA-grafted silica nanoparticle layers by manipulating pH and ionic strength, lateral electrostatic repulsions among the particles tend to inhibit close packing and make it difficult to eliminate adhesion between opposing surfaces. It is possible to produce mixed layers of PDMAEMA-grafted silica nanoparticles and PEO stars that pack tightly and eliminate adhesion. Moreover, we find that PEO stars and PDMAEMA-grafted silica nanoparticles are sufficiently attractive to associate with one another. This enables the layer-by-layer assembly of multilayer films of these materials. These films inherently have hierarchical structure, based on the assembly of 10 – 100 nm scale objects with polymer chains confined to central nanoscale cores. The cores and the brushes have distinct mechanical stiffness. Such films provide soft, long-range repulsions between surfaces, with no adhesion and low friction. This presentation will emphasize the relationship between film assembly conditions, film, and the nature of the normal and lateral forces between opposing films.

**COLL 42**

**Particle-sorption in wobbling polymer films**

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Mucus consists of sugar-chains in an aqueous liquid. It forms a soft, dilute polymeric barrier in e.g. the respiratory or intestinal system. This polymeric barrier acts as a filter allowing nutrient-uptake, while hindering the adherence and absorbance of bacteria and toxic materials. We aim at predicting particle-sorption in barrier-like solvated polymeric systems, such as gels and surface-anchored brushes, since it might ultimately aid in e.g. the design of efficient medication or help predict potential nano-toxicity of substances. We are specifically interested in the effect of out-of-equilibrium boundary conditions imposed by solvent flow and wobbling of the polymer film, because biological systems are constantly in motion. Here, I present our first steps towards predicting out-of-equilibrium particle-sorption in polymer brushes. Using coarse-grained molecular dynamics simulations and microfluidic experiments, we show that, depending on the shape, size and solvent-mediated particle-polymer interactions, particle sorption kinetics in brushes is slowed
down in the presence of continuous solvent flow, while it is enhanced when the solvent is refreshed via a batch-wise, stop-and-go procedure. Imposing oscillatory motion to the polymer film also enhances sorption kinetics.

**COLL 43**

**Influencing surface functionalization of aluminum fillers with acrylic-monomers through the onset of instability in Taylor Couette flow**

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Surface modification of metal fillers is a common approach to achieve a desired surface functionality while retaining the mechanical properties of the bulk material. Chemical functionalization of aluminum fillers with organosilanes, such as acrylic monomers, is an effective approach in modifying the fillers’ surface chemistry with specific (H₂C = C) functionality, leading to an increase in fillers’ affinity to polymer matrices. Understanding mixing characteristics and influence of flow behavior on mass-transport during such functionalization reaction is critical for the development of polymer-metal hybrid fillers with a uniform and well-characterized coating layer. As a model reactor system where flow takes place in the annulus between two concentric cylinders, Taylor-Couette flow allows for examining hydrodynamic instabilities while stimulating vortex motion, offering a highly active interface for mass transfer, and phase mixing.

This study explores the influence of vortex flow in tailoring the coating layer during the heterogeneous solid-liquid reaction involving the functionalization of aluminum fillers with Methacryloxypropyltrimethoxysilane (MPS) via liquid-phase silanization. Specifically, we focused on examining the effect of change in flow structure during the onset of primary instability in Taylor Couette flow, which results in the transition from purely azimuthal laminar flow to the emergence of Taylor vortices, on mass transport by characterizing the coupling efficiency (TGA), degree of coating and functionality (FTIR, XPS), coating thickness, uniformity and aggregation (Dynamic Light Scattering), roughness (AFM) and coating morphology (SEM).

Our analysis revealed that the emergence of vortex motion plays a critical role in offering a more uniform degree of coating, increased functionality, lower degree of aggregation, smoother surface and higher coupling efficiency. In addition, changing axial flow-rates allowed us to control the coating thickness, ranging between 15nm to 120nm.
Onset of Instability on surface chemistry

**COLL 44**

Current challenges in quantitative measurement of ligand binding and interactions at quantum dot surfaces

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As-synthesized colloidal quantum dot samples typically or inherently contain large concentrations of molecules that could coordinate the surface. We have prepared highly purified nanocrystal QDs using gel permeation chromatography, and we are using these QDs to study the effect of ligand association on quantum yield, quantitative measurements of ligand exchange and shell growth, and preparative use in the development of robust, biocompatible QD fluorophores. This talk will highlight recent results demonstrating the influence of ligand coverage on quantum yield and PL lifetime, measurement of QD-ligand binding interactions using isothermal titration calorimetry, and the preparation of biocompatible fluorophores using QDs with well-defined metrics.

**COLL 45**

Surface modification of inorganic oxide particles for improved dispersion in waterborne coatings

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Inorganic oxides used as pigments in waterborne coatings must disperse in both aqueous solution and hydrophobic films. Particle aggregation in both phases necessitates the use of large excesses of the energy-intensive pigments in commercial paint formulations. We have developed methods for improving oxide particle dispersion in both aqueous and organic media through accessible surface modification approaches. The dispersion stability of these modified particles is enhanced by associating with common dispersants. In addition, the modified particles are expected to improve film properties. These results and their implications for the sustainability of waterborne coatings will be discussed.

**COLL 46**

Colloidally suspended 3-MPA capped PbS quantum dots

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Quantum dot (QD) solar cells have recently seen rapid gains in efficiency (up to 9.9%) based on sequential layer-by-layer deposition and ligand exchange of PbS QDs with 3-mercaptopropionic acid (3-MPA) from their native oleate capping agent. Sequential deposition, while yielding increasingly efficient devices, results in material loss and disordered films. Additionally, while 3-MPA remains the ligand used in leading-efficiency devices, the interaction of 3-MPA with PbS QDs has primarily been limited to examination in QD solid arrays. Separately, colloidally suspended QD “Inks” have been targeted with the goal of deposition of highly ordered films and direct solution
processing with reduced material waste. We have prepared 3-MPA capped PbS QD colloids through a non-aqueous solution ligand exchange procedure starting with oleate capped PbS QDs. We report optical properties and ligand chemical structure to understand the interaction of 3-MPA with the QD core towards obtaining stable colloids for QD processing.

Figure 1. Absorption (solid traces) and luminescence (dotted traces) spectra of colloidal oleate and 3-MPA capped PbS QDs.

Figure 2. Solution 1H-NMR spectra of 3-MPA (A) before and (B) after ligation to PbS QDs.
Electrochemical characterization of selenium-modified gold surfaces

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Gold-selenium interactions afford stable and reproducible electroactive surfaces, which hold great promise for chemical and biological applications. Modification of electrode substrates with a selenium-based monolayer facilitates the study of solution analytes that would otherwise be impeded by surface chemistry. Using a combination of electrochemical and spectroscopic techniques, the behavior of selenocystine and its reactivity with physiological reductants has been characterized at modified gold substrates. Evidence for the formation of a selenium monolayer will be presented and a mechanism for the observed voltammetric profile proposed.

COLL 48

Smart materials based on thiol-functionalized pNIPAM and gold nanoparticles

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Light responsive polymers were prepared by covalently linking three types of thiol-functionalized thermally responsive N-isopropylacrylamide (NIPAM) polymers to gold nanoparticles (AuNPs). The first type, poly(NIPAM-b-NASI), consisting of blocks of NIPAM and N-acryloxysuccinimide (NASI), was synthesized by a two-step reversible addition-fragmentation chain transfer (RAFT) polymerization method employing 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid as the chain transfer agent (CTA). The pNIPAM-CTA homopolymer was prepared first and then subsequently used to polymerize NASI, which was post-functionalized with cysteamine. The second type, consisting of pNIPAM with a single thiol linkage at one end of the chain, was prepared by a one-step reaction between propylamide and the trithiocarbonate groups from a poly(NIPAM)-CTA homopolymer. The third type, a random copolymer between NASI and NIPAM, was synthesized using traditional radical polymerization techniques, then post-functionalized via cysteamine into poly(NIPAM-stat-cysteamine). Citrate-protected AuNPs, with average diameters of 10 nm, were attached to the thiol groups of the polymers using ligand place exchange reactions. The structures and compositions of the polymer/AuNPs solutions and their films were characterized by 1H-NMR, size exclusion chromatography, dynamic light scattering (DLS), ultraviolet/visible absorbance and X-ray photoelectron spectroscopies. Chemical vapor sensors and light-stimulated smart materials were fabricated from the polymer/AuNP composites by drop-casting them onto microelectrode arrays. The morphology of the films was studied using transmission and scanning electron microscopies. Their electrical conductivities in the presence of different vapors were found to change upon heating or laser irradiation, with the greatest change in
conductivity occurring when the laser wavelength matched the surface plasmon resonance of the AuNPs. The light-induced changes occur because of thermal energy transfer between the AuNPs and nearby polymers. The conductivity and laser responsiveness of the films are related to differences in the morphology that results from the polymer wrapping around the AuNPs. Possible applications of this work related to chemical sensing are discussed.

COLL 49

1-Adamantanethiol as a versatile nanografting tool

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Strategies to regulate the self-assembly of adsorbates to create surface structures with molecular-scale features and organization are of broad interest to nanoscience, biochemistry, and engineering. One approach utilizes molecules with tailored intermolecular interaction strengths and topologies to direct molecular self-assembly as exemplified by the adsorption of 1-adamantanethiol molecules on Au{111} substrates. 1-Adamantanethiolate self-assembled monolayers exhibit decreased packing densities and weaker intermolecular interaction strengths than n-alkanethiolate self-assembled monolayers, which result in their complete displacement upon exposure to n-alkanethiol molecules. Herein, we explore the capabilities of the AFM-based lithographic technique, nanografting, to fabricate chemical patterns comprised of 1-adamantanethiolate monolayers. Positive 1-adamantanethiolate patterns are generated by nanografting 1-adamantanethiol molecules into preexisting n-alkanethiolate self-assembled monolayers, and negative 1-adamantanethiolate patterns are created by nanografting n-alkanethiol molecules into preexisting 1-adamantanethiolate self-assembled monolayers. The patterned 1-adamantanethiolate regions are displaced upon exposure to solutions of n-alkanethiol molecules. This two-step nanografting-displacement strategy minimizes pattern dissolution as AD molecules do not intercalate into the preexisting SAM during nanografting. 1-Adamantanethiol can be utilized to create high-resolution sacrificial chemical patterns with feature sizes beyond those afforded other 1-adamantanethiol patterning strategies for applications such as resists for metallic and organic structures.
Programming the specific chemistry of single-site transition metal centers at surfaces by organic ligand design is a promising route to improve selectivity in surface catalysts. The chemical behavior of the surface and redox chemistry happening at the surface need to be further developed and understood. Our group has recently demonstrated the formation of structurally ordered and chemically uniform single-site centers at surfaces by on-surface redox chemistry of metallic precursors including platinum, chromium, iron, and vanadium with organic ligands on a gold surface (J. Am. Chem. Soc. 2014, 136, 9862-9865; J. Chem. Phys. 2015, 142, 101913; and newly submitted work). We report new results here that probe the extent of oxidation state control in these systems using tailored tetrazine-based ligands and vanadium metal, which is an excellent candidate for probing access to a variety of oxidation states. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined by X-ray photoelectron spectroscopy (XPS). Platinum(II) centers have also been formed with these ligands. In each of these cases, the metal-ligand complexes take the form of nearly identical one-dimensional polymeric chains, resolved by molecular-resolution scanning tunneling microscopy (STM). These structures provide highly uniform quasi-square-planar coordination sites for the metal, which contributes to the well-defined quasi-square-planar coordination sites for the metal. This strategy is also applied to earth-abundant metals such as iron and chromium using commonly available phenanthroline ligands and is allowing us to develop understanding of how to control and program single-site metal centers on surfaces for next-generation catalysis.


**COLL 51**

**Omniphobic bio-based coatings on polyolefinic substrates**

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A novel coating method is developed to protect polymeric substrates such as polypropylene (PP) films and fibers from the effects of solvents. This work utilizes the principle of biofouling to create a layer of bio-based polymers to activate the surface of PP. Soy proteins were identified as a suitable coating material, and were demonstrated to adhere rapidly and irreversibly onto PP. Upon activation the surface is amenable to further modification. We exploit the polyelectrolytic nature of bio-polymers to enable multilayer deposition with poly(diallyldimethylammonium chloride) (pDADMAC) and fumed silica nanoparticles on the negatively charged protein coating. After assembly, the fumed silica nanoparticles are functionalized by chemical vapor deposition with a fluoroalkyl silane, generating extremely low surface energy structures at the air-solid interface. This reduction of surface energy along with the corresponding increase in surface roughness due to nanoparticle adsorption results in superhydrophobic behavior (water contact angles greater than 160° and very low sliding angles) as well as increased contact angles with oils and alcohols.
Purification of carboxylated carbon nanotubes

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The conventional approach to functionalization of raw carbon nanotubes (CNTs) is via some form of acid treatment, which typically leads to over-functionalization and unwanted oxidation products. A majority of the functionalization schemes use acid treatment as a first step to introduce covalently bonded carboxylic functional groups on CNTs, which then can be further functionalized to amine, ester, amide, polymeric, or other groups. Dilute base-washing has been shown to remove oxidation debris by converting the acidic groups to their dissolvable conjugate salts. The microwave induced reactive base wash (MRW) is developed and found to be a better way to remove oxidation debris compare with conventional filtration method in terms of shorter reaction time and less reagent. In this work we present the effect of base-washing of carboxylated carbon nanotubes by both conventional filtration base wash and MRW. The effect on solubility, colloidal stability and surface functionalities are presented.
Eliminating ions from polyelectrolyte multilayers: A recipe high in salt

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Alternating deposition of polycations and polyanions on various surfaces results in versatile thin films termed polyelectrolyte multilayers (PEMUs). Depending on buildup conditions, certain PEMUs contain counterions which neutralize excess polymer charge. Since numerous PEMU properties, such as modulus, permeability and growth are controlled by ions, methods were explored to remove them or control their quantity. Because ions are introduced during PEMU assembly, post-buildup treatments based on charge compensation and salt annealing were explored. A technique to eliminate ionic content from a PEMU made of poly(diallyldimethylammonium chloride), PDADMAC and poly(styrene sulfonate), PSS will be presented. Multilayers were cycled between 2 M NaCl, a plasticizer that spreads the charges across the film, and a solution of PSS in lower salt concentration. PSS, which diffused more slowly than PDADMA in this system complexed with excess PDADMA near the surface without overcompensating. As a result, most ionic content was eliminated after a few cycles.

COLL 54

Lessons learned from inverse design of interactions for assembly

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Nanometer-scale, colloidally-stable particles suspended in a fluid can be driven to assemble into a wide variety of different structures depending on the control parameters of the system and the nature of the effective interparticle interactions. In many cases, the relevant interactions are tunable via external fields, physical or chemical modification of the particle surfaces, or changes in the composition of the suspending solvent. In this talk, we explore simple models for the "inverse" design of such interactions for cluster or superlattice forming systems. We also touch upon practical aspects associated with realizing and characterizing the designed structures.

**COLL 55**

**Thermal conduction by clustered colloids**

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The thermal properties of colloidal suspensions attracted attention about a decade ago, when studies announced large enhancements of the thermal conductivity, even at fairly low volume fractions. But subsequent studies muddled the picture with inconsistent reports of some times moderate and sometimes anomalously high enhancements. In all of these studies a key property that affects colloidal behavior, namely, the degree of clustering, was not controlled. Here we present a study using experiment, simulation and theory to quantify the effect of colloidal clusters on the thermal properties of a suspension. To accomplish this we have developed a colloidal system whose degree of aggregation can be controlled accurately and reversibly all the way from a state of fully dispersed nanoparticles to a state of a colloidal gel. We attach a silane on the surface of Ludox silica to produce nearly complete monolayer coverage. The coated particles are electrostatically stabilized at low pH, and fully gelled at basic pH under the action of hydrophobic interactions between the silane and the aqueous solvent. We control the cluster size via pH and use this system to measure the thermal conductivity of dispersions at fixed volume fraction of silica as a function of cluster size. We show that conductivity increases monotonically with size and it bound by the limits set by Maxwell's theory for conduction in inhomogeneous media. To quantify the effect of clustering, we develop an analytic model that treats clusters as microgels of finite size whose effective conductivity and volume fraction depend on structure. We show that this model gives very good agreement with the conductivity of simulated clusters and with experiment.
Nanodiamonds can be produced in large quantities via detonation synthesis, and when properly processed can be well dispersed in solution with a variety of different surface chemical terminations. The combination of large surface area, unique mechanical and optical properties of diamond, non-toxicity, and a variety of particle-substrate electrostatic interactions make nanodiamonds extremely useful for a wide-variety of applications in the materials and bio-medical sciences. These applications include drug delivery, cell imaging and toxin scavenging, as well as reducing friction and wear at sliding contacts.

We have been using a variety of experimental studies coupled with molecular simulation to understand and advance the application of nanodiamonds in lubrication and for reducing mold toxins in animal feed. This talk will review the results of these studies, as well as discuss new results relating the morphology and surface chemical functionalization to the solvation, correlated motion and lubrication mechanisms of nanodiamonds under shear flow. Support for these studies comes from the National...
Self-assembly simulations of polymer functionalized nanoparticles

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Functionalized nanoparticles have been the subject of a significant amount of research in a variety of fields. Their potential relevance to biomedical science arises from their ability to encapsulate therapeutic agents and deliver them to targeted cellular sites. The nanoparticles can be decorated with polymers to target specific sites or promote controlled aggregation for creating novel materials. We used coarse-grained molecular dynamics to simulate the aggregation dynamics of capsid-like nanoparticles grafted with polyethylene glycol (PEG) chains as well as nanoparticles grafted with PEG-poly(lactic acid) (PLA) diblock chains. We investigate the role of polymer grafting density and volume fraction on the aggregate morphology which is characterized by capsid coordination and cluster distributions. In addition, further analyses of cluster radius of gyration and principal moments of inertia provide morphology estimations near the microscale of the self-assembled structures.

Ghost tweezers method for studies of nanoparticle interaction with polymer brushes and lipid membranes

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We present an original method of “ghost tweezers” (GT) for coarse-grained simulations of NP interactions with complex interfaces. The GT method emulates lab experiments performed to manipulate nanoparticles and biomolecules with optical or magnetic tweezers. It is implemented into the dissipative particle dynamics simulation framework. GT represents a virtual harmonic potential, which tethers NP by a spring at a given distance from the interface. By moving GT, NP is driven to and through the interface, and the average force applied by GT to NP is measured. This force determined in quasi-static simulations is integrated to calculate the free energy landscape of NP-interface interaction and to determine the equilibrium adhesion states and the energy barriers between these states. The GT method is illustrated on two case study systems: a) interactions of bare and ligand-functionalized NPs with polyisoprene polymer brush in acetone-benzene binary
solvent and b) hydrophobic NP adhesion to and translocation through DPPC phospholipid membrane. We analyze different modes of NP adhesion, including partial and full immersion of NP into the polymer brush and internalization of NP by a lipid membrane, depending on NP size, hydrophobicity, and surface modification. The proposed GT method can be further implemented for modeling of nanoparticle behavior in various soft matter and biological systems.

**COLL 59**

### Multiscale modeling of polymers

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Macromolecular systems have interesting behavior on a range of length-scales and timescales. Computational study of these systems therefore requires modeling at multiple levels of detail. The development of coarse-grained (CG) models for macromolecules is an exciting and challenging frontier of research in computational chemistry. The ultimate goal is to develop a model that is computationally feasible but captures the essential physical chemistry. I will discuss our recent efforts in this area. We have developed a CG model of water called the big multipole water (BMW) model which is in the spirit of the MARTINI model (four water molecules are grouped into one site) but includes electrostatic interactions including a quadrupole moment. I will discuss the performance of this force field for several problems including the properties of polymers in solution, the interaction of polymers with nanoparticles, and the adsorption of nanoparticle coated with polymers to membrane. The results demonstrate the importance of electrostatic correlations in the water model, and suggest that these models can be useful in investigating complex fluids over long length-scales.

**COLL 60**

### Towards the virtual laboratory: modelling clay-polymer nanocomposites using a multiscale approach

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We have developed an advanced multiscale simulation system to predict the properties of polymer-clay nanocomposites based on their molecular structures and composition. These methods could have applications in modelling a wide range of materials and it is our aim to create a “virtual lab” to compute the properties of new soft materials based simply on knowledge of their chemical composition, molecular structure and processing conditions [1]. Here we will present our findings from modelling chemically specific combinations of clay and polymers, where we use our multiscale methods and tools to take us from a parameter free quantum description to atomistic and coarse-grained
simulations, ultimately leading to predictions of the materials properties of these nanocomposites. Our simulations approach realistic sizes of clay platelets (diameter 100 Å) at low clay volume fractions (5%). These systems exhibit property enhancements compared to the pristine polymer (elastic properties, gas permeation), but homogenous dispersion of the clay sheets is required.

Our multiscale approach provides us with predictions of the melt intercalation behaviour and final morphologies of montorillonite clay – polyvinyl-alcohol and montorillonite clay – polyethylene-glycol systems, and associated organic-treated clays. Many hitherto unobserved phenomena come into view as a result of this study, including the dynamical process of polymer intercalation into pristine and organo-treated clay tactoids and the ensuing aggregation of polymer-entangled tactoids into larger structures. We observe the role of surfactants and are able to elucidate how it facilitates polymer intercalation and ultimately clay sheet exfoliation, which is driven by attraction to the clay surfaces.

From our multiscale simulations, we can compute various characteristics of these nanocomposites, including clay-layer spacings, out-of-plane clay sheet bending energies, X-ray diffractograms and materials properties, which we relate to the system's final morphology.


COLL 61

Controlling non-covalent dispersion of hydrophobic objects with lipids and polymers

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Phospholipids and phospholipid derivatives offer efficient, noncovalent functionalization and dispersion of hydrophobic objects, e.g. therapeutic molecules and nanoparticles including carbon nanotubes (CNTs). However, the relation of lipid aggregates in bulk solution and in the presence of the object, and the resulting dispersion remain important questions. Here, we examine by combining molecular simulations, theory, and experiments aggregates at interfaces and the resulting non-covalent solubilization of CNTs via amphiphilic lipids [1] or block-copolymers [2,3].

By varying the molecular shape and CNT size, we find the assembled morphology transitions from micellar-like to tubular coating with phospholipids [1] and micellar to monolayer-like with longer polymers [2]. We show that the transition depends mainly on the amphiphile curvature with respect to CNT diameter and that it drastically changes the dispersive effectiveness of the coating. This allows us to fine-tune CNT dispersion via changing the amphiphile shape. We connect the simulational findings with
theoretical approximations for these coatings either by Helfrich bending considerations (phospholipids) or by polymer scaling theories (polymers). Finally, we show the differences in coating dispersive effectiveness leads into assembly differences and enhanced antimicrobial ability of layer-by-layer films functionalized by dispersed CNTs in our experiments [3].


COLL 62

Quantitative electrochemical detection of analytes at sub-picomolar levels using a simple paper sensor

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The objective of the project described in this presentation is the creation of new, low-cost, appropriately sensitive paper universal diagnostic devices for the electrochemical detection of analytes ranging from biological weapons to DNA to biomarkers characteristic of organ function in the human body. To satisfy this objective, we initiated development of a quantitative sensor using a magnetic microbead supported silver nanoparticle metalloimmunoassay. The sensor integrates picomolar affinity antibodies (or DNA) with our easily handled, but sophisticated, electrochemical detection platform: the NoSlip. This device exhibits quantitative electrochemical detection of analytes present at sub-picomolar levels using non-enzymatic signal amplification. Total assay time is < 3 min and matrices include urine and blood. The cost is ~$1/sensor.

COLL 63

Electrochemical protease profiling toward cancer analyses using peptide-functionalized carbon nanofiber nanoelectrode arrays

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Here we report the development of an electrochemical method for rapid profiling of protease activities through monitoring the proteolytic kinetics of ferrocene (Fc)-labeled-tetrapeptides that are immobilized at the exposed tips of nanoelectrode arrays (NEAs) fabricated with vertically aligned carbon nanofibers (VACNFs). Using alternating current voltammetry (ACV), an enhanced AC current signal of Fc can be clearly extracted and followed in time, reflecting the proteolytic activity of specific proteases that cleave the peptides. The detection of the activity of a cancer related protease, cathepsin B, has been demonstrated with purified recombinant cathepsin B in buffer solutions and spiked in human tissue lysates. An algorithm based on heterogeneous Michaelis-Menten model has been developed. This algorithm has been further validated in detecting cathepsin B activities in complex breast cell lysates. Four types of breast cells have been tested, including normal breast cells (HMEC), transformed breast cells (MCF-10A), breast cancer cells (T47D), and metastatic breast cancer cells (MDA-MB-231). The detected protease activity was found increased in cancer cells, with the MDA-MB-231 metastatic cancer cell lysate showing the highest cathepsin B activity. The equivalent cathepsin B concentration in MDA-MB-231 cancer cell lysate was quantitatively determined by spiking recombinant cathepsin B into the immunoprecipitated MDA-MB-231 lysate and the HMEC whole cell lysate. The results illustrated the potential of this technique as a portable multiplex electronic device for cancer diagnosis and treatment monitoring through rapid profiling the activity of specific cancer-relevant proteases. It can be also used as an analytical platform for screening effective protease inhibitors as potential cancer drugs.

The catalytic cleavage to the peptides functionalized at the exposed tip of vertically aligned carbon nanofibers embedded in SiO2 is monitored with AC voltammetry and used to derive the activity of specific proteases.
Nucleic acid biosensing at interfaces: Physicochemical perspectives and future prospects

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Solid phase hybridization is performed in thousands of research studies annually as well as, increasingly, for clinical applications. This talk will briefly overview the current state of technologies based on solid phase hybridization, discuss physicochemical aspects of hybridization as encountered in interfacial environments, and provide suggestions on how these technologies can be advanced beyond current capabilities. Features of hybridization on solid supports and how it relates to the better understood case of solution hybridization will be addressed, as will prospective benefits of using materials other than DNA for the immobilized "probe" species. Next generation technologies should aim to suppress biases from analyte folding, markedly shorten assay times, obviate the need for enzymatic processing of samples, and work directly with unlabeled, minimally-processed analyte.

COLL 65

Aptamer-functionalized chemomechanically-modulated biomolecule catch-and-release system

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The efficient extraction of (bio)molecules from fluid mixtures is vital for applications ranging from target characterization in (bio)chemistry to environmental analysis and biomedical diagnostics. Inspired by biological processes that seamlessly synchronize the capture, transport and release of biomolecules, we designed a robust chemomechanical sorting system capable of the concerted catch-and-release of target biomolecules from a solution mixture. The hybrid system is composed of target-specific, reversible binding sites attached to microscopic fins embedded in a responsive hydrogel that moves the cargo between two chemically-distinct environments. To demonstrate the utility of the system, we focus on the effective separation of thrombin by synchronizing the pH-dependent binding strength of a thrombin-specific aptamer with volume changes of the pH-responsive hydrogel in a biphasic microfluidic regime, and show the non-destructive separation with quantitative sorting efficiency, system’s stability and amenability to multiple solution recycling.
Using electrochemical DNA-based (E-DNA) sensors to monitor cooperative DNA-protein interactions

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Electrochemical sensing platforms have shown significant use in the quantitative detection of target molecules with high sensitivity, reproducibility, and selectivity. Particularly, electrochemical DNA (E-DNA) sensors, which typically use surface-bound single-stranded oligonucleotides modified with a redox active molecule on the distal end, have been employed in the detection of various targets (e.g. small molecules, proteins, DNA, etc.) based on target-induced flexibility changes occurring within the
DNA structure that alter the efficiency of electron transfer between the redox active molecule and the electrode surface, thus, allowing for quantitative detection of target concentration. To date, a number of studies on E-DNA sensors have shown their selectivity, sensitivity, and quantitative power in detecting molecular targets; however, no studies have shown the ability of this class of collision-based sensors to elucidate biochemical-binding mechanisms such as cooperativity. In this study, we demonstrate that E-DNA sensors modified with different lengths of a surface-bound oligodeoxythymidy late [(dT)ₙ] (n = 7, 14, 21) sensing probe are able to quantitatively differentiate between cooperative and non-cooperative binding of gene 32 protein (g32p) - a single-stranded DNA-binding protein that exhibits cooperativity upon binding to single-stranded DNA. Specifically, we demonstrate that oligo(dT) E-DNA sensors are able to detect g32p down to the nM level (50 nM – 4 μM), as well as exhibit signals capable of distinguishing between the cooperative binding of the full-length g32p and the non-cooperative binding of the core domain (*III) fragment to single-stranded DNA. We also show that this binding is both probe length- and ionic strength-dependent. Thus, this study illustrates a new quantitative property of this powerful class of biosensors and represents a rapid and simple methodology for understanding DNA-protein binding mechanisms.

COLL 67

To model chemical reactivity in heterogeneous emulsions: Think homogeneous microemulsions

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We have demonstrated that pseudophase kinetic models that work in association colloids also describe observed rate constants and reactant distributions in kinetically stable emulsions just as they do in homogeneous microemulsions. Over 20 years ago, William Porter aptly characterized then current knowledge about antioxidant efficiencies in aqueous organized media and non polar oils as the polar paradox: i.e., nonpolar or amphiphilic antioxidants tend to function better in organized media, e.g., emulsions or membranes of high surface to volume ratios while polar antioxidants are more efficient in bulk lipids. This apparent paradox and the difficulty in determining antioxidant distributions in emulsions made the selection of the best antioxidant for a particular application for scientific reasons difficult. Here we show our solution to this problem. Pseudophase kinetic models work in homogeneous microemulsions and emulsions for two reasons: the totality of each region—oil, interfacial and aqueous— in microemulsions can be treated as separate reaction regions without considering microemulsion or emulsion droplet size. The diffusivity of the reactants are near the diffusion controlled limit such that after bulk mixing their distributions are in dynamic equilibrium between the oil, interfacial and aqueous regions in homogeneous microemulsions or in kinetically stable or stirred emulsions throughout the time of the reaction being studied.

This talk will include: (a) the basic assumptions of the pseudophase kinetic model as
applied to microemulsions and emulsions; (b) the important properties of the hydrophobic arenediazonium ion probe; and (c) two methods for monitoring reactions in opaque, fluid emulsions, dye derivatization and linear sweep voltammetry, and example results, e.g., antioxidant partition constants between the oil and interfacial and aqueous and interfacial regions of the emulsions and the rate constant for reaction in the interfacial region. Together the results demonstrate that the chemical kinetic method provides a unique, versatile, and robust approach for determining the effect of emulsion properties such as oil hydrophobicity, emulsifier structure, temperature, droplet size, surfactant charge, and pH on partition constants. The chemical kinetic method also provides a natural explanation for the, until now, unexplained “cut-off” effect, a sharp drop in antioxidant efficiency with increasing alkyl chain length of a particular antioxidant.

COLL 68

Understanding co-surfactant-sophorolipid combinations for improved interfacial properties

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Sophorolipids are biosurfactants that are fermented from renewable feedstocks and have attracted considerable interest as an alternative to the synthetic surfactants currently in use. Natural sophorolipids, however, have solubility and emulsification limitations. Previous work by our group has shown that by using simple green chemical modifications, modified sophorolipids can be made with greatly improved surface and interfacial tension properties as well as emulsification activity.

In practice, surfactants are rarely used alone in a final application. This is often to take advantage of the positive characteristics of multiple surfactants while overcoming their limitations. Sophorolipid derivatives have shown exemplary interfacial tension properties but difficulties have been encountered with adsorption and solubility. In order to overcome these limitations two different types of co-surfactants were introduced; n-alkyl alcohols, ranging in length from 2 to 22 carbons, as well as sophorolipid derivatives of other lengths.

To understand the effect of the sophorolipid-derivative co-surfactant pairs, surface tension, interfacial tension, and emulsification were studied. Interaction parameters between the co-surfactants were measured based on air/water surface tension and oil/water interfacial tension. Diffusion and adsorption coefficients of each surfactant pair was measured based on dynamic interfacial tension data. Changes in emulsification resulting from the surfactant pair was measured by observing phase stability and particle size. Interestingly, it was found that the co-surfactant pairs not only changed the surfactant properties that were expected such as adsorption and stability, but also properties such as solubility and foaming.
Location and influence of added block copolymers on oil-in-oil emulsions

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We have investigated the effect of added polystyrene-b-poly(ethylene oxide) (SO) copolymer on the stability of oil-in-oil (O/O) emulsions containing polystyrene (PS) and poly(ethylene glycol) (PEG) in chloroform (CHCl\textsubscript{3}), and directly visualized the location of SO in the emulsions by using dye-labeled SO (SO*) with confocal laser scanning microscopy (CLSM). The emulsion formed by PS/PEG/CHCl\textsubscript{3} = 14/6/80 (wt %) consisted of a droplet phase of PS in CHCl\textsubscript{3}, and a continuous phase containing PEG in CHCl\textsubscript{3}. SO*s with various molecular weights (\(M_n,SO\)) and volume fractions of the PS block in SO (\(f_{PS}\)) were prepared via living anionic polymerization and subsequent end-esterification. The effect of SO on the droplet size in the emulsions was investigated as a function of both \(M_n,SO\) and \(f_{PS}\). Increasing \(M_n,SO\) and decreasing \(f_{PS}\) were effective in reducing the droplet size down to less than 1 μm, which is 100 times smaller than in the absence of SO. The location of SO*s in the O/O emulsions were further investigated by CLSM. We found that the location of SO*s changed from the droplet interior, to the interface, and then to the continuous phase with decreasing \(f_{PS}\). We discuss the possible mechanism in terms of the relation of SO* location to the droplet size.

Thermodynamic approach to interfacial concentration gradients

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We present a novel thermodynamic approach to the description of concentration gradients associated with interfaces in solutions of surface active species. The approach identifies a characteristic lengthscale for the spatial extent of the concentration gradient, and demonstrates that it can be derived from macroscopically-observable factors such as surface tension. The approach can be applied both to the adsorption of surface active molecules and to the distribution of ions about a charged surface. The results offer insight that can aid in the interpretation of many phenomena related to the behavior of solutions about interfaces and porous solids.

New generation of smart surfactants for miniemulsion
Nanocarriers synthesized by inverse (water-in-oil) miniemulsion are important for the mild and orthogonal encapsulation of various payloads like drugs, proteins or nucleic acids. As emulsions have to be stabilized with surfactants and frequently block copolymers are used (for steric stabilization) of the droplets, which however, have some drawbacks: they can be difficult to synthesize and / or to remove after the reaction or formulation. Also biocompatibility is a major concern as they are amphiphilic macromolecules. We produced new surfactants, which consist in a homo or block copolymer with protecting groups. These protection groups are necessary to generate a low hydrophilic-lipophilic balance, which is needed for the stabilization of a water-in-oil system and show an efficient stabilization during the nanocontainer synthesis. After the nanocarriers are formed, they have to be transferred into an aqueous dispersion. At the same time, the protection group is cleaved to create a completely water-soluble polymer. Thus a stable nanocontainer dispersion with a low amount of surfactant is produced which is optimal for further biomedical purposes.

Figure 1. Homo or block copolymers with protecting groups as new surfactants in inverse miniemulsion to stabilize nanocarriers.

Dynamically reconfigurable complex emulsions via tunable interfacial tensions
Emulsions have proven of critical importance for research and application within a multitude of fields ranging from the medical sciences to the food industry. Control over a complex emulsion’s physical and chemical properties is paramount to achieving the desired functions and applications. A longstanding goal has been the development of robust and scalable methods allowing high-volume and rapid fabrication of complex emulsions with highly controllable structure, including both multiple emulsions and Janus emulsions. We describe a novel approach to the bulk fabrication of complex liquid droplets utilizing temperature-induced phase separation of hydrocarbon, silicone, and fluorocarbon liquids (Zarzar, L, D. et al, *Nature*, 2015, 518, 520-524). The geometry of the emulsion droplets can be meticulously tuned between encapsulated and Janus configurations as controlled through different mixtures of surfactant or by stimuli-responsive surfactants such as those sensitive to pH or light. The geometry of these droplets can be accurately predicted and explained by theory. We anticipate that the newfound ability to reversibly alter the morphology of complex droplets will have significant impact across the multitude of fields which already employ emulsions as well as open new areas of research utilizing such droplets as dynamic materials.

The morphology of hexane (H) and perfluorohexane (F) droplets in water (W) can be alternated between encapsulated and Janus configurations. Here, droplets transition from F/H/W double emulsions stabilized by 0.1% sodium dodecyl sulfate into H/F/W double emulsions as the concentration of Zonyl FS-300 fluorosurfactant increases. Zonyl diffuses from right (high concentration) to left (low concentration).

**COLL 73**

**Understanding the interactions of epoxides and amines as reactive compartments in aqueous dispersions**
The presented work focuses on transferring the reactivity of two component systems to a one component concept. Therefore, we investigated the interaction of two highly reactive nanocompartments in aqueous dispersions, especially focusing on how to suppress their reaction. Epoxide resins and polyamines that show immediate crosslinking upon contact were chosen for this study. Initially emulsified separately, the two dispersions were mixed and colloidal stability could be maintained. Destabilization of the amine emulsion droplets especially could be avoided by introducing a new type of crosslinkable surfactant which undergoes spontaneous polyaddition at the droplet interface, as shown by isothermal titration calorimetry (ITC). [1] The formation of the desired epoxy-amine polymer network is simply triggered by film formation and evaporation of the solvent, causing the emulsions to interdiffuse and react. Additionally, the system is interesting for self-healing applications. To achieve this we prepared nanofibers by colloid electrospinning to encapsulate both compartments in one polyvinylalcohol (PVA) fiber which was confirmed with dual-colour STED microscopy. The fibers showed self-healing ability triggered by thermal and mechanical stimuli. [1] Bijlard, A.-C.; Winzen, S.; Itoh, K.; Landfester, K.; Taden, A. ACS Macro Letters 2014, 3, (11), 1165-1168.

Figure 1: Schematic presentation of the “pseudo” one component epoxy-amine system
Investigating surfactant-based oil recovery process in reservoirs with heterogeneous mineralogy

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Oil contamination is one of the major environmental concerns today. To eliminate this problem, environmental friendly surfactants are used to wash out the adsorbed oil on the rock surface. In addition, the interfacial properties of aqueous surfactant solutions with oil have direct impact on enhance oil recovery (EOR) processes. Therefore, several works have been dedicated to evaluate the efficiency of different surfactant on various mineral surfaces.1 However, to the best of our knowledge, no study has been conducted using rocks having heterogeneous mineralogy. Considering the heterogeneity is important since sediments rock samples formed from igneous rocks are compose of different minerals. The goal of this study is to investigate the performance of different surfactants in heterogeneous reservoir considering the wettability alteration of each mineral.

To this aim, first, we mapped the surface mineralogy of the rock sample using Scanning electron microscopy images and Energy Dispersive X-Ray analysis Spectroscopy (EDX). To choose the most effective surfactants, then, we determined the phase behavior of 10 different nonionic, environmental-friendly surfactants in binary mixture of oil and water. Subsequently, HRTEM imaging was used to characterize micro emulsions of oil and surfactants. Furthermore, the critical micelle concentration (CMC) each surfactants in brine determined by pendant drop method. We determined the wettability of each mineral present in the rock sample by measuring contact angle of brine+surfactant/mineral surface. The performance of these surfactants was then monitored through spontaneous imbibition tests with the rock samples saturated by oil. To study the effect of the wettability alteration on the experimental results, we aged the minerals and core sample in the crude oil for 10 days and repeated the contact angle and imbibition tests.

Framboidal triblock copolymer vesicles: A new class of efficient Pickering emulsifier

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A series of poly(glycerol monomethacrylate-block-2-hydroxypropyl methacrylate-block-benzyl methacrylate) framboidal triblock copolymer vesicles (denoted as G63-H350-Bz for brevity; where the mean degree of polymerization of the third block, z, is systematically varied from 21 to 373) were prepared via RAFT seeded emulsion polymerization of benzyl methacrylate using a linear G58-H300 vesicle precursor. These framboidal vesicles were characterized using TEM, DLS and small-angle x-ray scattering (SAXS) and then evaluated as Pickering emulsifiers for the stabilization of n-dodecane droplets in water. The additional hydrophobic character conferred by the poly(benzyl methacrylate) block is sufficient to stabilise the vesicles during high shear, allowing adsorption at the oil/water interface as intact vesicles. A turbidimetry assay was used to determine the vesicle adsorption efficiency as a function of increasing surface roughness. The adsorption efficiency increased from 36 % up to 94 % when z was increased from 21 to 125, but remained relatively constant at higher z values. Hence there is a strong positive correlation between surface roughness and Pickering adsorption efficiency. Moreover, this represents a significant improvement in Pickering emulsifier efficiency compared to that reported previously for non-framboidal cross-linked copolymer vesicles [J. Am. Chem. Soc., 2012, 134, 12450].
Characterizing the effect of modification on cellulose nanocrystal pickering emulsions

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Cellulose is one of the most common biomacromolecules on the planet and is produced by many organisms from plants to certain sea creatures to some bacteria. It is well known that controlled acid hydrolysis can selectively remove amorphous domains of cellulose leaving highly crystalline rod-like cellulose nanocrystals (CNCs). CNCs are completely renewable, biodegradable, and have a large surface area (greater than 100 m$^2$/g) with hydroxyl functionalities that are readily modified.

CNCs are usually manufactured by strong acid hydrolysis using sulfuric or hydrochloric acid that results in their irreversible aggregation upon drying due to hydrogen bonding. By the appropriate surface modification of CNCs, their aggregation can be reduced or
eliminated. Thus far most surface modifications are performed in solvent and involved lengthy and impractical solvent exchange steps. Our laboratory is developing concurrent one-pot Fischer Esterification/acid hydrolysis reactions to prepare functionalized CNCs. This allows for the tuning of CNC surface hydrophobicity that is important to their use as Pickering emulsifiers.

CNCs were modified with levulinate and citrate groups, and the effect of surface chemistry on Pickering emulsions was investigated. They were emulsified with paraffin oil at various concentrations. Emulsions’ pH and ionic strength were varied to evaluate the effect of formulation parameters on the modified CNC performance as a Pickering emulsifier. Emulsions were aged for 24 hours and then the particle size was measured by dynamic light scattering and physical stability was recorded. CNC modification in addition to altering pH and ionic strength of the medium drastically affects their emulsification performance.

COLL 77

Multibody coalescence in Pickering emulsions

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Particle-stabilized Pickering emulsions have shown unusual behaviors such as the formation of non-spherical droplets and the sudden halt of coalescence between individual droplets. Here, we report another unusual behavior of Pickering emulsions – the simultaneous coalescence of multiple droplets in a single event. Using latex particles, silica particles, and carbon nanotubes as model stabilizers, we show that multi-body coalescence can occur in both water-in-oil and oil-in-water emulsions. The number of droplets involved in the $n^{th}$ coalescence event equals the corresponding number of the tetrahedral sequence in close packing. Furthermore, coalescence is promoted by repulsive latex and silica particles but inhibited by attractive carbon nanotubes. The revelation of multi-body coalescence is expected to help better understand Pickering emulsions in natural systems and improve their designs in engineering applications.
Size distributions of three types of Pickering droplets. Results of different analyses are organized in columns: (a, b, c) diameter histograms showing distinctive maxima: $d_n$’s ($n = 0, 1, 2, 3$), (d, e, f) inverse correlations of $d_n$’s with stabilizer-to-droplet mass ratio $a$, and (g, h, i) linear correlations of $d_0$’s ($n > 0$) with $d_0$.

Scaling of Pickering droplet diameters according to the tetrahedral number sequence.

**COLL 78**

**Multicompartmental colloids: Synthesis, properties, and function**
The area of colloidal science has witnessed the emergence of a wide spectrum of colloidal particles with novel attributes, such as shapes, surface patterning or internal compartmentalization over the last decade. In our hands, electrohydrodynamic co-jetting has resulted in a range of different nano- and microparticles with controlled interfacial patchiness, and a wide range of different shapes. In contrast to methods that selectively surface modify isotropic particles, electrohydrodynamic co-jetting can yield colloids where the particle bulk can be designed to exhibit intrinsic anisotropy. The simplest variation is a colloid where its two hemispheres are comprised of two different bulk compositions with the potential to contain distinct payloads of drugs or dyes in both compartments. Thus, these particles may exhibit a combination of otherwise hard to combine, often orthogonal, properties within the same particle. An example is a "colloidal surfactant", where one hemisphere is hydrophobic and the other hemisphere is hydrophilic. The emergence of interfaces in such colloids leads to a wealth of new functions ranging from microactuators to controlled release formulations.


**COLL 79**

**Conformation and diffusion of DNA-coated nanoparticles**

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DNA-coated nanoparticles are widely studied as a basic building block for programmable three-dimensional architectures. A crucial ingredient for their use in such applications is a thorough understanding of their dynamic and conformational properties. Via a variety of computer simulation techniques we explore their conformations in solutions of mono- and multivalent salt, their dynamics in polymer solutions as a function of DNA grafting density as well as solution properties, and their behavior near surfaces.

**COLL 80**

**Colloidal nanomaterials-encapsulated microcapsule for biomolecular sensing**

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Non-invasive implantable sensors that are able to continuously detect and monitor targeting biomolecules in vivo are needed for early diagnostics of disease. Although many colloidal nanomaterials have been developed as optical sensors to detect biomolecules in vitro, they are not suitable to directly introduce into human body as implantable sensors. One potential solution is incorporating the nanosensors in hydrogel scaffold, yet the direct contact between the nanosensors and the hydrogel tends to disrupt the performance and sensitivity of the nanosensors. In this work, a novel microcapsule-based sensing platform was presented to prevent the direct contact between delicate nanosensor surface with the hydrogel matrix. Colloidal nanosensors were encapsulated in polyethylene glycol microcapsules with liquid cores, which were fabricated by forming water-oil-water template double emulsion using microfluidic techniques. Confocal fluorescence microscope technique confirms that the microcapsules have tunable permeability to glucose and heparin, while the nanosensors are trapped inside the capsules without leaking out. Glucose-responsive quantum dot or gold nanorod sensors, or heparin-responsive gold nanorod, were encapsulated in the microcapsules respectively. These nanosensors-loaded microcapsules showed responsive optical signals in the presence of targeting biomolecule such as glucose or heparin. Furthermore, these microcapsules can be immobilized in biocompatible hydrogel as implantable materials for biomolecular sensing. The versatility and universality of this technique offer new opportunities to extend the utility of colloidal nanosensors from solution-based detection to implantable device-based detection.
Power-free mechanochromic sensors from force-recording, elastoplastic inverse opals

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Athletes, soldiers and even normal people could sustain a concussion or traumatic brain injury as a result of exposure to a certain type of mechanical force in sports or in accidents. It would be ideal if we could develop a power-free, wearable patch that can change color immediately and the appeared color can correspond to the level of the mechanical force. Photonic crystals are dimensionally periodic dielectric structures exhibiting a photonic stopband that determine the wavelength of reflected light. The displayed color can be tuned by varying the particle size, lattice spacing, volume filling fraction and refractive index contrast within the porous network. Many have created polymeric inverse opals that can be responsive to external stimuli to change colors.
However, few can record the mechanical force in real-time or the recorded force is rather small. Here, we created inverse opals as mechanochromic patches by backfilling the colloidal crystals of silica particles (diameter of 320, 285, and 238 nm) with thermoplastic photoresist, SU-8, followed by removal of the templates. Due to elastoplastic deformation of SU-8 films, the deformed inverse opals do not fully recover, allowing us to establish the relationship between the mechanical force and optical responses. The patches are highly sensitive; $\Delta\lambda/\Delta\varepsilon$, the ratio of shift in the stopband wavelength to the change in applied strain, is 5.7 nm/%, the highest compared to literature data. When the normal forces of 30, 60, and 90 mN are applied to the pristine inverse opal (320 nm), the stopband blue-shifts to 570, 500, and 440 nm, respectively, corresponding to the pore diameter of 292, 263, and 233 nm, respectively, in good agreement with the pore size in the [111] direction, 297, 262, and 227 nm obtained from SEM images.

To reveal the underlying deformation mechanisms as well as the overall mechanical responses of the inverse opal of SU-8 under different loads, we carry out micromechanical modeling using the finite element method (FEM). The simulation results corroborate well with experiments, suggesting that the uniform variation in pore geometry under the compression play a key role in determining mechanochromic property. The inverse opals prepared from SU-8 can be potentially used as power-free mechanochromic sensors to measure the magnitude of shockwaves without the need of complicated instrumentation for in-situ imaging.

COLL 82

How do surfaces alter the structure in multicomponent polymer systems and vice versa? A computer simulation study

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Using computer simulation of soft, coarse-grained models we study the structure, thermodynamics, and kinetics of structure formation of mixed polymer brushes, copolymer brushes and copolymer-nanoparticle mixtures. The softness of the interactions and the implicit representation of the solvent allow for a computational efficient simulation of a variety of polymer structures and thermodynamic conditions (solvent quality, temperature and pH value), and it enables us to study experimentally large invariant degrees of polymerization. Additionally the particle-based description facilitates to describe the correlation between the molecular dynamics of the macromolecules and the collective kinetics of structure formation. Three applications illustrate the versatility of the model:

a) We model the temperature-sensitive swelling behavior of poly(N-isopropylacrylamide) (PNIPAM) polymer brushes using a third-order virial expansion for the non-bonded interactions, validate our model by comparison to experimental findings, and investigate the structure of mixed brushes that incorporate various amounts of poly(ethylene glycol) (PEG). Opportunities for designing the architecture of these mixed PNIPAM-PEG
brushes as temperature-responsive biomolecule-absorbing surfaces are discussed.

b) We investigate the response of adaptive multicomponent polymer brushes (PAA-b-PS copolymer brushes and PAA/PS mixed brushes) to chemically patterned top surfaces as a function of the solvent quality and grafting density of the brushes. The role of the geometry and scale of the surface pattern is explored and related to the response of the spontaneously assembled morphologies of the brushes without adsorbed top pattern.

c) The structure formation of copolymer-nanoparticles is investigated as a function of the interaction between the nanoparticles. The role of the kinetics of self-assembly is studied for parameters where the nanoparticles are smaller than the characteristic size of the copolymers and their volume fraction is large.

Response of a mixed brush to a stripe pattern for various solvent qualities.

**COLL 83**

**Tortuosity and branching of worm-like micelles accessed by small-angle neutron scattering**

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In aqueous solution, surfactants usually self-assemble to spherical or ellipsoidal micelles at concentrations slightly above the CMC. At high concentrations or in presence of salt, these structures can become elongated and adapt rod-like shapes. At even higher surfactant or salt concentrations, extended and tortuous assemblies of
rods, so called worm-like micelles (WLMs), are formed. WLMs exhibit unique viscoelastic properties and find vast employment in e.g. liquid soaps or as drag reducers. A thorough structural characterization of WLMs can be difficult, because the length scale of the structural features ranges from the nanometer regime for the radius of the local cylindrical geometry up to micrometers for the contour length. Small-angle neutron scattering has proven to be an excellent tool to determine these structural parameters. We developed a new scattering function, which accounts for the local cylindrical geometry as well as the global tortuous structure. Moreover the presence of branches can be detected and quantified. The properties of the function will be discussed and exemplified with results from an anionic surfactant system.

Artificial biomembrane models using giant vesicles comprised of amphiphilic random block copolymers

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The biomembranes of intracellular organelles have their own lipid compositions that determine the membrane curvature, thickness, and shape of the organelle. With the aim of establishing artificial models for the biomembranes employing the giant vesicles, the morphological changes in the vesicles based on the composition of the mixed amphiphilic copolymers and the coexistence of a segment copolymer as the sterol model, coupled with the fabrication of a microvillus-like structure were explored using the amphiphilic poly(methacrylic acid)-block-poly(methyl methacrylate-random-methacrylic acid) random block copolymer, PMAA-b-P(MMA-r-MAA), prepared by the photopolymerization-induced self-assembly.

The mixed copolymers with different lengths of the hydrophilic PMAA blocks for a constant length of the hydrophobic P(MMA-r-MAA) block varied the morphology depending on the composition. Large contorted vesicles formed by the copolymer having a short PMAA block were changed into smaller spherical vesicles due to the coexistence of the copolymer having a middle PMAA block (PMAA-M), via the formation of more severely contorted vesicles with an increase in the PMAA-M composition. Micro-sized spherical vesicles produced by only the PMAA-M copolymer were transformed into worm-like vesicles, followed by key-shaped vesicles with the increasing composition of the copolymer having a long PMAA block. The spherical vesicles formed by PMAA-M were changed into a planar bilayer in the presence of a sterol model using a P(MMA-r-MAA) segment copolymer that had the MMA/MAA ratio and length identical to those of the hydrophobic block of the PMAA-b-P(MMA-r-MAA). A thermal analysis demonstrated that the segment copolymer was intercalated between the hydrophobic block chains of the block copolymers in the vesicle cores and disordered the hydrophilic surface of the PMAA blocks. Furthermore, the PMAA-b-P(MMA-r-MAA) copolymer produced a microvillus-like structure as observed in digestive systems and glands. The microvillus structure was obtained on the surface of a film formed by the precipitation of the worm-like vesicles. The finger-like structure in the microvilli had an ca. 8.5 μm length, being shorter than the ca. 20-μm length of the finger structure in the microvilli of a gall bladder.

These studies imply that specific and unique structures based on the lipid composition in living bodies can be fabricated using non-natural polymer amphiphiles.

**COLL 85**

**Sliding tethered ligands: Lock and key colloidal interactions with a topological twist**

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Specific adhesion is mediated by specific lock and key interactions between ligand-receptor pairs. The complementary moieties are anchored to the substrates by ubiquitous tethers that control the interaction range and the mobility of the ligands and receptors, allowing for an efficient tuning of the kinetics and strength of the binding events between colloidal or biological interfaces. In this work, we add topological
interactions to the toolbox of ligand-receptor design by developing a family of tethered ligands for which the spacer can slide at the anchoring point. Our results show that this additional sliding degree of freedom changes deeply the nature of the adhesive contact, in particular by extending the spatial range over which the binding forces may sustain a significant value. The introduction of sliding tethered ligands with self-adjustable length paves the way for the development of versatile specific adhesion substrates that can better accommodate surface roughness and dynamic fluctuations.

COLL 86

Thermal stabilization effect of multilayer graphene-coated metal nanostructures

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Due to their nanoscopic dimensions, metallic slanted columnar thin films have significantly reduced melting temperatures when compared to bulk material as described by the Gibbs-Thompson equation. A conformal several-layer graphene coating, grown by a low-temperature chemical vapor deposition process, is shown to increase the thermal stability of the nano-columns. In this work, we show that cobalt and titanium slanted columnar thin films can be coated with carbon films, which protects the morphologies of the nano-columns at temperatures that damage their uncoated counterparts.

COLL 87
First principles simulations of pure water

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Experimentally there is an ongoing debate regarding the structure of pure liquid water at ambient conditions. One set of experimental data suggests that over 80% of hydrogen bonds are existent in liquid water giving it a crystalline tetrahedron structure similar to solid water. Other experimental data says that only 20% of hydrogen bonds exist in water making the system seem more like a disorderly liquid. In this project, Ab Initio Molecular Dynamics (AIMD) and statistical mechanics were used to study the structural and dynamical properties of pure water at ambient conditions. Two different density functionals Perdew-Burke-Ernzenhof (PBE), Becke-Lee-Yang-Parr with an empirical correction (BLYP-D3), and one force field, Q-TIP4P, were used to describe the system.

The system conditions were constructed in a periodic boundary cube containing 32 water molecules. The VASP code was used to run simulations. The calculations were run using Lawrence Livermore National Laboratories computer clusters. A canonical ensemble was used for Q-TIP4P simulations.

Some disadvantages when running computer simulations for pure water are that most functionals over structure water at ambient conditions. Also, PBE describes water as having a density of 0.85-.90 g/cm³ and an extremely high melting point of approximately 400 K. The functionals also lack quantum nuclear effects which are observed in the radial distribution functional results for oxygen-hydrogen.

Here we present the impact of these approximations on structural properties such as the radial distribution functions, tetrahedrality parameters, hydrogen bond (HB) angles, and percentage of broken HB’s in liquid water.

It is seen that the BLYP-D3 functional and the Q-TIP4P yield a less over-structured liquid than PBE with a smaller molecular dipole moment and a higher number of broken HB’s. HB’s give us an idea of how structured the liquid is. If the liquid has a high number of HB’s it appears to be more like a solid. PBE gave a value of 72% HB, BLYP-D3 48% and Q-TIP4P 43%, which tells us how disordered the liquid is.

We hope to extend the methods to study ion solvation in pure water with H3O⁺ and OH⁻. We are also interested in using different functionals in our simulations with more accurate descriptions for dispersion forces and calculate structure factors for all of the functionals.

COLL 88

Flame-retardant surfaces from green vinyl ester resin

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Use of composite materials for construction of DoD weapons platforms will approach 200 million pounds per year. VER is a low-cost resin that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composite structures such as ship hulls and transportation vehicles. The objective of this work is to make flame retardant surfaces by developing an environmentally safe "green" vinyl ester resin (GVER) from renewable biomass wastes. Lignin was obtained from waste wood and pulp production, while glycerin was obtained from animal fat, biodiesel production, and/or from waste vegetable oil of the food industry.

**COLL 89**

**Molecular modeling and DFT analysis of theoretical covalent cross-linkages between hydroxyproline stereoisomers and galacturonic acid**

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Hydroxyproline rich glycoproteins such as extensin exist in covalent and ionic cross-linkages with pectic polysaccharides such as polygalacturonic acid in the cell walls of many plants. Polygalacturonic acid, polymeric β-(1-4) linked D-galacturonic acid, contributes to cell wall rigidity and elasticity through interactions with serine, arginine, and hydroxyproline residues of structural proteins. In the present study, theoretical covalent linkages between 4-hydroxyproline and galacturonic acid were modelled and characterized using atomistic level electronic structure calculations. The effect of hydroxyproline stereochemistry on stability of the theoretical complexes was also explored. Electrostatic potential maps were rendered and used to study potential interactions between galacturonic acid and hydroxyproline monomers. Galacturonic acid was linked via glycosidic, amide, and ester linkages to (2S, 4S)-4-hydroxyproline and (2S, 4R)-4-hydroxyproline. Models were minimized with density functional theory using the EDF2 6-31G* potential in implicit water. Hydrogen bond formation and changes in Gibbs free energy, ΔG, were used in the characterization of the proposed theoretical covalent linkages.

**COLL 90**

**Long range nanoruler for cancer cell sensing**

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For scientists in different disciplines, the optical ruler has served as an important tool to address a wide range of biological activities. Since the state of the art FRET rulers is limited to 10 nm distance, developing long range optical ruler became very important to monitor the biological processes beyond the FRET limit. With this need, the current study reports for the first time the design of long-range two-photon induced scattering spectroscopy ruler using gold nano-antenna separated by a bifunctional rigid double strand DNA, which controls the length of the ruler. Reported data demonstrate that TPS spectroscopy ruler's working window is within 25 nm distance, which is more than twice that of well recognized FRET. The possible mechanism for the long range two-photon spectroscopy ruler capability has been discussed using angle-resolved TPS measurement and FDTD simulations. Solution phase experimental data conclude that a long-range TPS ruler using A9 aptamer can be used for screening of prostate specific membrane antigen (PSMA) (+) prostate cancer cells even at 5 cells/ml level. Reported result with PSMA (−) normal skin HaCaT cells indicate that TPS ruler based assay has the capability to enable distinction from non-targeted cell lines. Finally, the long range TPS ruler can be used towards the better understanding of chemical and biological processes beyond FRET limit.

Magnetic-nanoparticle conjugated hybrid graphene oxide for prostate cancer detection and treatment

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According to the United States Centers for Disease Control and Prevention, prostate cancer is one of the leading causes of death among men in the United States, second only to lung cancer. It is now well known that the detection of circulating tumor cells (CTCs) is an invaluable tool for early diagnosis and monitoring the progression. However, since in the early stage of cancer, a very few CTCs exist among billions of erythrocytes, clinical doctors need extremely sensitive methods to detect them. Motivated by this need, magnetic-nanoparticle conjugated theranostic graphene oxide (GO) was developed for targeted capture of prostate CTCs, accurate diagnosis, and combined therapeutic action against prostate cancer. The experimental results show that anti-epithelial cell adhesion molecule (EpCAM) antibody and A9-aptamer-attached flower-shaped magnetic nanoparticle-bound 2D graphene can be used for selective capture, enrichment and label-free multicolor fluorescence imaging of LNCaP prostate cancer cells from infected blood. Also, the experimental data clearly demonstrate that indocyanine green (ICG)-conjugated A9-aptamer-attached theranostic GO is capable of external near-IR 785 nm light-driven combined synergistic photothermal and photodynamic treatment of prostate cancer. Comparative studies to demonstrate the efficacy of the heranostic GO material design were conducted.
Fabrication of stable, low-density, self-assembled monolayers on gold by click thiol-yne reaction

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Self-assembled monolayers have tremendous impact in interfacial science, due to the unique opportunity they offer to tailor surface properties. Low-density self-assembled monolayers are an emerging class of monolayers where the environment-interfacing portion of the adsorbate has a greater level of conformational freedom when compared to traditional monolayer chemistries. This greater range of motion and increased spacing between surface-bound molecules offers new opportunities in tailoring adsorption phenomena in sensing systems. In particular, we expect low-density surfaces to offer a unique opportunity to intercalate surface bound ligands into the secondary structure of proteins and other macromolecules. Additionally, as many conventional sensing surfaces are built upon gold surfaces (SPR or QCM), these surfaces must be compatible with gold substrates. Here, we present the first stable method of generating low-density self-assembled monolayer surfaces on gold substrates. Our approach is based on the 2:1 addition of thiol-yne chemistry to develop new classes of y-shaped adsorbates on gold, where the environment-interfacing group is spaced laterally from neighboring chemical groups. This technique involves an initial deposition of a crystalline monolayer of 1,10 decanediethiol on the gold substrate, followed by grafting of a low-packed monolayer on through a photoinitiated thiol-yne reaction in presence of light. Orthogonality of the thiol-yne chemistry (commonly referred to as a click chemistry) allows for preparation of low-density monolayers with variety of functional groups. To date, carboxyl, amine, alcohol, and alkyl terminated monolayers have been prepared using this core technology. Results from surface characterization techniques such as FTIR, contact angle goniometry and electrochemical impedance spectroscopy confirm the proposed low chain-chain interactions of the environment interfacing groups. Reductive desorption measurements suggest a higher stability for the click-LDMs compared to traditional SAMs, along with the equivalent packing density at the substrate interface, which confirms the proposed stability of the monolayer-gold interface. In addition, contact angle measurements change in the presence of an applied potential, supporting our description of a surface structure, which allows the alkyl chains to freely orient themselves in response to different environments.

COLL 93

Efficient removal and killing of multidrug-resistant Staphylococcus aureus (MRSA) using polycyclic antibacterial peptide-functionalized 3D porous graphene oxide membrane

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According to the World Health Organization (WHO), a high percentage of hospital-acquired infections are caused by highly resistant bacteria such as multidrug-resistant *Staphylococcus aureus* (MRSA) or multidrug resistant gram-negative bacteria. These bacterial infections are a massive threat to human health. Since bacteria evolve to resist antibiotics faster than scientists can develop new classes of drugs, the development of new materials which could be used, not only for separation, but also for effective killing of drug resistant pathogens is urgent. To overcome this problem, we have designed and synthesized the nisin-functionalized polyethylene glycol (PEG)-conjugated three dimensional (3D) porous graphene oxide membrane for identification, effective separation, and complete killing of multidrug resistant *S. aureus* from water. Experimental data show that due to peptide binding affinity, MRSA is captured by the porous membrane, allowing only water to pass through. SEM, TEM, and fluorescence images confirm that pathogens are captured by the membrane. RT-PCR data, along with colony counting, indicate that almost 100% of MRSA can be removed and destroyed from the water sample using the porous membrane. Comparison of MRSA viability data of nisin alone, graphene oxide membrane alone, and nisin-attached graphene oxide membrane demonstrate that nisin antimicrobial peptide-attached graphene oxide membrane can dramatically enhance the possibility of destroying MRSA due to the multiple interactions between the peptides and bacteria.

**COLL 94**

**DFT study of formaldehyde coupling reaction on rutile TiO₂ (110) surface**

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Oxygen vacancy sites on rutile TiO₂ (110) have been shown to play important roles in the coupling reaction of the adsorbed formaldehyde molecules of the surface. An important intermediate for the formation of C₂H₄ is believed to be the adsorbed diolate (-OCH₂CH₂O-). In the present work, we report our DFT study of the possible mechanisms of formaldehyde coupling reaction. In particular, we found three different diolate species on the defective TiO₂ (110) surface (Figure 1). By comparing the adsorption energies and the C-O bond breaking energies, we attempt to map out the most favorable reaction pathways for C₂H₄ formation.
Alpha-ketoglutaric acid for neutralization of hydrazine and monomethylhydrazine waste streams

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Hydrazine and monomethylhydrazine (MMH) are hypergolic fuels widely used in the aerospace industry as rocket propellants. These fuels are highly reactive and toxic, having potentially carcinogenic properties, leading to strict regulations on handling, transport, and disposal to protect workers and the environment. Previous research studies have confirmed the effectiveness of alpha-ketoglutaric acid (AKGA) as a potential alternative to conventional disposal methods to convert these toxic fuels into stable organic products through an irreversible reaction. This presentation focuses on chemical kinetics studies, effects of common interferences, and biodegradability of products for the reaction of hydrazine and monomethylhydrazine with excess AKGA solution. Products formed from the reactions are 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (mPCA) respectively. Using a 15:1 excess of AKGA, pseudo-first order kinetics were determined at low concentrations of the hydrazines. In an effort to develop a cost-effective system, the ratio of AKGA:hypergol was lowered and second order kinetic rate constants (first order in both reactants) were determined. Kinetic studies of lower AKGA: fuel ratios (as low as 1.1:1) with higher hydrazine concentrations (1%) were performed, resulting in acceptable degradation efficiencies for a potential field-scale test. Hydrazine
degradation was rapid with the hydrazine concentration converted to PCA within 12 minutes with a 2:1 AKGA: hydrazine ratio. Under the same conditions, MMH degradation results showed slower kinetics than hydrazine but still converted to mPCA within 2 hours. Biodegradability of the products were accessed in an effort to verify the safety of releasing the products to an industrial waste water treatment facility. This data will be used to assess the viability of these reactions for a scaled-up test as an environmental friendly approach to treat hydrazine and MMH contaminated waste streams.

**COLL 96**

**Surface-enhanced Raman spectroscopic (SERS) detection with submonolayer nanoparticle arrays**

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Conducting nanoparticles with plasmon resonances create local, nanoscopic field enhancements that increase the surface-averaged SERS cross-section of an analyte molecule by orders of magnitude (the enhancement factor EF). Realistic chemical sensing would take advantage of the excellent SERS selectivity, while requiring high average EF over large substrates for practical sampling. Novel sub-monolayer arrays (NMAs) of unusual nanoparticles with large field enhancements, designed and fabricated at the US Army Natick Soldier Research, Development, and Engineering Center (NSRDEC), demonstrated EF > $10^6$ over large (~ cm$^2$) areas, when coated with a benzenethiol (BT) standard. NMAs could potentially be used for detecting chemical agents (CAs) as part of an appropriate sensor system.

NSRDEC has developed a simple model for the signal-to-noise ratio obtained during SERS measurements of airborne analytes. A “sticky” NMA would collect airborne CAs by adsorbing molecules during time $t_{exp}$. EF (a function of the nanoparticles, their array spacing, and the excitation wavelength) and the sticking or binding coefficient $S_i$ (a function of the molecules, surface, airflow, temperature, and vapor pressure) are important parameters. $S_i$ can vary over eight orders of magnitude, and may depend on nanoparticle shape, size, and configuration, so is best to characterize experimentally. The density of analyte molecules on a surface $NA$, is proportional to concentration $C_m$ (determined by vapor pressure and distance from the source) times sticking factor $S_i$ times $t_{exp}$. The number of signal photons $S$ is given by the product of EF and $NA$ (the areal density of Raman-scattering molecules), the system’s optical efficiency, the excited area, the integration time of an inexpensive CCD, incident flux of laser photons in photons/cm$^2$, etc. Using typical excitation power density and collection areas, we obtained the minimum detectable concentration as a function of both $S_i$ and EF. For an analyte molecule with EF = $10^6$, and $t_{exp} = 10$ s, $S_i$ must be more than $3x10^{-4}$ to achieve ppt detection. Our analysis may help determine whether low-vapor pressure materials can be detected at all in the gaseous state, enabling better understanding, modeling,
and predictions of agent interactions (sticking factor/binding energies, reaction energies, vapor pressure, etc.), with different materials (polymers, metals, particles, etc.).

**COLL 97**

**Tunable thermochromism of anthraquinone induced by reversible microparticle/nanoparticles switching in blended block copolymers**

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We present a novel thermochromism behavior based on crystallization of anthraquinone dyes with the assistance of pluronic. At high temperature, the hydrophobic anthraquinone dye was dispersed in pluronic solution as nanoparticles whereas at low temperature, the dyes formed microcrystals driven by the dye-dye and dye-pluronic molecular interactions. The crystallization process altered the optical properties of dye with bathochromism accompanied with change of color. We found the thermochromism was fully reversible. The pluronic not only solubilized the hydrophobic dye, but also changed the crystallization process and morphology of microcrystals by tuning the molecular interactions. We found the crystal formation-melting turning point is in exact agreement with the critical micellization point (CMT), suggesting the thermocromism is CMT related. Therefore, the thermochromism could be readily tuned by changing the CMT of pluronic aqueous solution, which could be changed easily by using different concentrations of pluronic or blending different pluronics.

**COLL 98**

**Characterization of surface area burial upon formation of biomolecular interfaces**

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Salts and uncharged solutes exert a wide range of effects on condensed phase processes, ranging from protein folding and viral capsid formation to the osmotic regulation of kidneys. All of these seemingly disparate processes involve large changes in water-accessible surface that can be quantitatively analyzed using a simple molecular thermodynamic model. The resultant interaction coefficients for solutes with biologically-relevant functional groups highlight intermolecular interactions important for biological function. We have constructed a database of biological molecules from the protein databank to systematically investigate burial of molecular surface. We discuss qualitative trends in terms of predicted salt and osmolyte interactions with the predominant surface area types buried in the formation of secondary structure, folding, and crystallization.

**COLL 99**
Control of radiation sensitivity of inorganic resists by exchanging ligands

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Hafnium oxide sulfate, Hf(OH)_{4-2x-2y}(O_2)_x(SO_4)_y·qH_2O, known as HafSOx have received attention as one of the promising next generation inorganic resists due to its high resolution and low line width roughness (LWR). However, HafSOx system is suffering from its high background condensation and relatively low radiation sensitivity compare with organic photoresists. In this study, we exchanged the radiation insensitive sulfate for oxalate. By mixing peroxy-oxalato-niobate with HafSOx system, we could minimize the radiation insensitive ligands and introduced more radiation sensitive ligands to the system. Because both of HafSOx and peroxy-oxalato-niobate are stable in acidic condition, mixture of both clusters didn’t precipitate and remain a clear solution. The thin film made of this mixture has been patterned by electron beam lithography. The results showed the radiation sensitivity shifted apparently to lower energy with maintaining the contrast.

COLL 100

Development and characterization of surface modified metal oxide nanoparticles

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Metal oxide nanoparticles are interesting candidates as precursors for novel materials in a wide range of electronic devices. However, manufacturing electronic components with nanoparticles often leads to inhomogeneity or the lack of structural control. Surface modification of the metal oxide nanoparticles can increase the suspendablity of the particles in solution allowing for their orderly introduction into larger structures. This work details the systematic evaluation of various surface treatments and conditions to optimize suspendablity and incorporation into diverse thin film and bulk materials. The formation and uniformity of the surface treatments were analyzed and validated by the introduction of optical probe molecules within the modification layers. The extent of surface coverage and structural data was determined using FTIR, XRD, SEM-EDX, and refractometry.

COLL 101

Tuning surface chemistry on layer-by-layer nanoparticles to target ovarian cancer
The layer-by-layer functionalization of nanoparticles allows for the incorporation of any strongly charged polymer into a nanomaterial, thereby providing an impressive breadth of possible surface chemistries to choose from when designing a nanotherapeutic. Our group has previously demonstrated that biopolymers adsorbed onto the surface of LbL nanoparticles retain the ability to interact with their binding partners on the surfaces of cells, such as in the case of hyaluronic acid and the CD44 receptor. Here we explore a variety of novel surface functionalizations using the LbL approach, generating a small library of particles with coatings that include biocompatible polymers such as poly(L-glutamic acid) (PG), dextran sulfate, heparin sulfate (HS), hyaluronic acid and poly(propargyl-L-glutamate) (PPLG). In addition to unmodified polymers, we explore the impact of chemically conjugating known targeting moieties such as folate to PG, HS, and PPLG. We analyze the in vitro uptake of these particles in several ovarian cancer cells lines that includes SKOV3, COV362 and CAOV3, and evaluate their in vivo stability and biodistributions using a xenograft model of ovarian cancer.

COLL 102

Temperature-dependent SPR measurement of the influence of probe density on the denaturation temperature of hybridized DNA on surfaces

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The hybridization activity of DNA probes on surfaces with DNA targets in solution has been widely studied. What is less known are the factors that influence the thermodynamic stability of hybridized DNA structures on surfaces, such as the surface density of probes. To address this question we have developed a strategy for immobilizing single-stranded DNA probes on gold surfaces and a method for analyzing their temperature dependent hybridization properties. Gold surface plasmon resonance (SPR) sensors were functionalized with DNA probes using an attachment strategy based on preferential adsorption of phosphorothioated adenine nucleotides. This strategy allows a wide range of probe-to-probe spacings be realized on the surface. The SPR-based methods allow efficient measurement of the hybridization activities of these probes and the thermal stabilities of the hybrids formed with these probes over the range 30 °C to 70 °C. The results allow us to determine how the thermal denaturation temperature of DNA hybrids varies with probe spacing.

COLL 103

C₆₀-functionalized flavin (FC₆₀) toward nanotube-based photovoltaics
The potential roll-to-roll, low-cost fabrication of organic photovoltaics has become increasingly attractive for power generation to even the most remote locations. P3HT (poly(3-hexylthiophene)) and PCBM ([6,6]-phenyl-C-61-butyric acid methyl ester) are the most widely used donor/acceptor materials in organic photovoltaics (OPVs). One of the biggest challenges of organic semiconductors is their low charge carrier mobility. The four to five orders of magnitude higher charge carrier mobility of semiconducting (sem-) single walled carbon nanotubes (SWNTs) can potentially address this issue, if one manages to appropriately configure them in heterojunction structure with the proper carrier extraction architecture. To this effect, the supramolecular organizations of flavin mononucleotide (FMN) around single walled carbon nanotubes (SWNTs) was shown to provide effective nanotube dispersions and the ability to impart selective enrichment of sem-SWNTs by recognizing the underlying nanotube helical pattern. Utilizing this approach, we herein present our recent work in outfitting the organic analogue of FMN (FC12) with a terminal PCBM functionality. The presence of PCBM moiety provides an effective photoluminescence (PL) quenching for both FC60 and FC12-dispersed SWNTs with ca. 1% incorporated FC60. Spectroscopic characterization enable to verify the incorporation of FC60 within the FC12 helix. The suggested system here helps to improve homogeneous environment around the SWNTs and SWNT individualization which can promote exciton dissociation and then single layer processability of organic photovoltaics.

COLL 104

Thermodynamics of ionic liquid polymer solutions

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 Ionic liquids (ILs), organic salts that are fluid at ambient conditions, are a novel class of compounds with a combinatorially great chemical diversity and unique properties. The very low volatility and high thermal and chemical stability that many ILs exhibit, render them promising as solvents. We consider ionic liquid + polymer + water systems, where we investigate using isothermal titration calorimetry the interactions between ionic liquid and water and between ionic liquid and polymer, and also the polymer phase behavior under different solvent conditions. This research supports and guides applications of ionic liquids in formulated or functional products.

COLL 105

Influence of structure and surface passivation on photoluminescence intensity and rate dispersion in core/shell quantum dots
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Photoluminescence (PL) is an important property of colloidal semiconductor quantum dots (QDs) for applications as QD-based light-emitting diode and bio-labeling agents. Quantum yield and PL lifetime are strongly dependent on structures, surface traps and ligand passivation. In this work, the influences on PL for wurtzite CdSe/CdS core/shell QDs with well-defined core size, shell thickness, surface ligand types/densities will be discussed. The core sizes and shell thicknesses are controllable via selective ionic layer adhesion and reaction (SILAR) based techniques. Clean initial QD surfaces can be achieved by gel permeation chromatography (GPC) to facilitate comparison of the impacts of post-introduced ligands. Multiple types of passivation ligands such as trioctylphosphine oxide, oleylamine, trioctylphosphine, cadmium oleate are examined to understand the mechanism for enhancing photoluminescence. Support plane analysis methods are used to describe PL decay in terms of several characteristic lifetime components, and the results are used to constrain models for quenching/enhancement of PL emission.

COLL 106

Pralidoxime functionalized polydiacetylene for colorimetric detection of organophosphates

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Due to the hazardous effect of organophosphates contamination, well-developed approaches that could rapidly detect, identify and detoxify organophosphates, either chemical warfare agents (CWA) or pesticides are necessary. Colorimetric detection is among the most convenient and readily accessible detection methods. In the present work, we designed a p-conjugated polymer system based on polydiacetylene(PDA) for a rapid, sensitive and selective colorimetric detection of organophosphates. The structure of diacetylene monomer consists of four parts: hydrophobic lipid tail, diacetylene triple bonds, conjugation carbon chain, and the terminal functional group. As an amphiphilic molecule, diacetylene monomers self-assemble into a vesicle, micelle or tubular structure in aqueous milieu. Polydiacetylene is formed from 1,4-addition photopolymerization of self-assembled diacetylenes, resulting in a highly ordered conjugated backbone. After the photopolymerization, hydrophobic lipid tails are wrapped inside while the functional groups are exposed outside. The optical property of polydiacetylene results from its p-conjugated backbone electron resonance. Polydiacetylene molecules have maximum absorption at 630 nm and 550 nm. These
peaks correspond to a mixture of blue (630 nm) and red (550 nm) colors observable by naked eye. Polydiacetylene possesses a unique ability to change colors in solution or suspension which enables its application in sensors. By attaching an oxime alpha-nucleophilic group to the carboxylic terminus of polydiacetylene, we imparted an organophosphate-binding ability to the pralidoxime assemblies. We conceptualized that the pralidoxime-modified PDA (PDA-PAM) would be selective toward certain organophosphate esters. Herein, we report on the synthesis, vesicle formation and characterization, and colorimetric properties of the PDA-PAM. The rapid reaction between pralidoxime and malathion induced twist of the p-conjugated PDA backbone to produce a rapid and sensitive colorimetric change. The developed PDA-PAM based sensor assay can be conveniently prepared by simple self-assembly of the diacetylene monomers and UV irradiation. The PDA-PAM vesicle suspension is capable of producing rapid, sensitive and specific response to organophosphate malathion, while a PDA-PAM solution shows a naked-eyes detection range from a few mM to mM and a PDA-PAM-modified Teflon membrane has the detection limit of several nmols per cm².

COLL 107

Quantification of viral surface lipids using plasmon-coupling based UV-Vis spectrophotometry

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Specific lipids on the surface of viruses have been found in recent years to be playing important roles in their infection process. In the case of HIV-1, phosphatidylserine and gangliosides such as G₃₃ have been shown to contribute to the attachment and entry of the virus particles to various host cells. Therefore, the ability to quantify these surface lipids seems to be crucial in understanding the underlying mechanisms and finding therapeutic strategies against such viral diseases. Conventionally, mass spectrometry has been used as a precise method for lipid quantification. However, it suffers from the complicated sample preparation and relatively large sample sizes which cannot easily be provided by patient samples. We have recently developed a plasmon coupling microscopy-based technique which takes advantage of DNA-conjugated metal nanoparticles as probes and allows for clinically-relevant sample sizes, yet provides a precise quantification. Since the microscope sample preparation, measurement and data processing in this method requires some sophistication, we have simplified this technique by replacing the microscopy with UV-Vis spectrophotometry. This has given us the opportunity for a simpler and more time-efficient quantification procedure which only slightly compromises in precision. The assay works based on the reaction of biotinylated metal nanoparticles and liposomes or virus-like particles surface-functionalized with biotinylated cholera toxin B and neutravidin in colloid. In this presentation, I will report the latest results of this project including the calibration of the assay on standard G₃₃ liposomes with gold and silver nanospheres that provide different sensitivities and its application to HIV-1 virus-like particles.
Coll 108

Fundamental catalytic studies of bimetallic and oxide nanomaterials for CO oxidation and the reverse water gas shift reaction

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The size effects of reactive metal particles supported on a Au(111) substrate were investigated by ultrahigh vacuum, temperature programmed desorption/reaction (TPD/R) for their use as catalysts in the reverse water gas shift reaction (RWGS) and carbon monoxide (CO) oxidation. Systematic studies originated with metallic Ti nanoparticles on Au in an effort to elucidate the dependence of molecular adsorption on the size and position of the nanoparticles, thereby probing the closely knit structure/activity relationship of the material. These studies extend to the investigation of oxide particles on Au(111) by exposing the metallic Ti nanoparticles to an oxygen environment to form titania particles. The size of the oxide nanoparticles is optimized for the greatest chemical activity for CO oxidation, while catalytic size effects are monitored. Unraveling the reactivity and structural relationship in model catalysts will aid the future design of novel catalysts.

Coll 109

Protein adsorption on silica nanoparticles and oxidized silicon: Effect of surface wettability and chemistry

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Design of protein repellent, biocompatible nanoparticles as well as flat surfaces have been explored for various application in pharmaceutical, agriculture and food processing industries. Chemistry and wettability of the surfaces play an important role in biocompatibility, especially the adsorption of proteins. Silica nanoparticles, with individual particle diameters of 10-20 nm and oxidized single crystalline silicon surfaces were modified to render them either hydrophilic or hydrophobic. Hydrophilic surfaces with different surface chemistries were prepared by attaching: a) polyethylene glycol silane (PEG) or b) a zwitterionic siloxane (sulfobetainesiloxane or SBS) to the surface. Hydrophobic surfaces were prepared by coating the nanoparticles/oxidized silicon with dimethyl dichlorosilane (DMDCS) via a chemical vapor deposition method. Modified surfaces were characterized by Raman spectroscopy, thermogravimetric analysis (TGA) and contact angle goniometry before and after exposure to protein solutions. Protein adsorption on the different nanoparticles was studied by UV-Vis spectroscopy using bovine albumin serum (BSA) and fibrinogen as model proteins. On oxidized silicon
surfaces, XPS, confocal microscopy and contact angle measurements were used to characterize protein adsorption as a function of time.

Maximum protein adsorption was observed on hydrophilic silica surfaces whereas almost no protein adsorption was observed on PEG and SBS coated hydrophilic silica surfaces. Due to the non-wetting nature of the hydrophobic nanoparticles, almost no protein adsorption was detected as the particles do not disperse in aqueous solutions. To study protein adsorption on a surface with the same chemical functionality, but no roughness, flat silica surfaces were prepared using the same techniques. These flat hydrophobic surfaces showed protein adsorption at a level intermediate between hydrophilic treated and untreated oxidized silicon surfaces. Coating of hydrophilic silica nanoparticles and oxidized silicon with PEG or SBS was shown to be an effective approach to design biocompatible protein repellent surfaces without affecting the initial wettability.

**COLL 110**

**Role of tyrosines within Amot as a driver for protein-lipid association**

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Amot proteins have been shown to control cell proliferation and differentiation and can selectively bind with high affinity to phosphoinositol containing membranes. This binding event is linked to endocytosis, changes in cellular polarity, and apical membrane sequestration of nuclear transcription factors associated with development of cancer phenotypes. Although the lipid selectivity of the protein has been well characterized, the mechanisms involved in the Amot coiled-coil homology domain (ACCH) binding these membranes have not been fully described. Several techniques including lipid sedimentation, fluorescence resonance energy transfer, peptide-tiled spots blotting, and mass spectrometry have been used to probe for residues responsible for lipid association. The combination of these approaches suggests that there are 4 lysines and 3 arginines responsible for driving this interaction. In the FRET assays, the native fluorescence was used to characterize the binding event. For these assays, we used a mutant where each tyrosine which had significantly different binding constants compared to the wild type protein was mutated into a phenylalanine. Therefore each experiment measured FRET from a single fluorescent probe within the protein. However, differences in binding affinity for each tyrosine could be a result of differences in ability to insert into the membrane. To determine, the role of tyrosine membrane exposure in protein binding affinity, we endeavored to study short peptides containing the sequence surrounding each of the 5 tyrosines. 2-3 amino acid peptides, 15-mer peptides, and full domain mutants were compared for the ability to be shielded by various hydrophobic environments (alcohol study), hydrophilic environments
(sugar study), or amphiphilic environments (liposome study). Characterizations of these shifts with respect to what is seen with the various tyrosine-phenalanine mutants will further our understanding of whether each tyrosine is buried within the protein or interacts with the membrane

**COLL 111**

**Effect of aromatic and hydrophobic interactions in amphiphilic supramolecular assemblies in response to temperature changes**

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Micelle-like supramolecular assemblies are significantly employed in diverse fields of science and technology. Herein, we investigated the effect of incorporating aromatic functional groups into the hydrophobic moiety of facially amphiphilic dendrons on self-assembly, where we systematically probed different hydrophobic units with aromatic and non-aromatic functional groups while keeping the hydrophilic part constant. According to our experimental results and molecular dynamics simulation data, we show that the stability of the micellar assembly is greatly influenced by hydrophobicity as well as aromaticity. We found that dendritic assemblies are more dynamic and less stable upon temperature changes when hydrophobic units of the dendron lack aromatic group. On the contrary, the stability of the dendritic assembly is significantly improved when we incorporate the aromatic functional group into the hydrophobic moiety of the supramolecular structure. These results will have an impact on to the rational design of supramolecular assemblies with controlled properties.

**COLL 112**

**Size- and shape-controlled synthesis of gold nanoparticles using chitosan as a stabilizer**

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In recent years, gold nanoparticles (AuNPs) have been extensively studied due to their favorable colloid stability, good biocompatibility and tunable surface modification chemistry. Chitosan, an ideal material in the biomedical and biotechnologies fields, have been used as a polymeric stabilizer to synthesize zerovalent gold nanoparticles, which can be widely used in sensors, drug/DNA delivery and imaging. Herein, we report size-and shape-controlled synthesis of AuNPs functionalized with chitosan as polymer stabilizer in the presence of halide ions (F\(^-\), Cl\(^-\), Br\(^-\)) by controlling Temperature, pH, and
chitosan concentration. Considering the excellent conjugation of folic acid and chitosan, FA-chitosan functionalized AuNPs can be extensively applied in target CT imaging, and even target bioimaging and drug delivery fields.

**COLL 113**

**Stimuli-responsive nanomaterials for detection and active decontamination of chemical and biological threats**

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The development of responsive finishes and materials for defense against chemical and biological threats can be accomplished via the modification of textiles, such as cotton and expanded nanostructured fluoropolymer membranes. When properly modified, these substrates can serve as self-decontaminating systems that protect against vaporous threat agents, as stimuli-responsive systems that actuate or react when triggered by an external signal, and/or as sensors that detect the presence of threat agents. Our work involves the integration of catalysts, silica nanostructures, and responsive polymers into a textile substrate. Catalysts that facilitate the detoxification of chemical/biological threats that our group has had success with—8-hydroxyquinoline, 1,2-benzisothiazol-3(2H)-one, and Rose Bengal. All of these catalysts are “dual-use”, meaning they protect against both chemical and biological threats, as well as provide protection from ambient pathogenic infections. In addition, the catalysts are relatively non-toxic, environmentally friendly, commercially available, and approved for use for other applications. The challenge is to integrate the catalyst into a useable textile substrate to produce a stable, durable finish that can withstand several washes and a range of environmental conditions while retaining a reasonable shelf and service life. The finish should also autonomously protect from incoming threats, i.e, the protective properties are enhanced in the presence of the appropriate environmental trigger. In this work, we show that this decontamination process can be enhanced by incorporating signal-responsive polymers into a silica/catalyst matrix. Such polymers respond to environmental stimuli—such as pH change—via physical transformation which, in turn, can change the surface energy, porosity, and/or promote the release of decontaminants or other functional molecules. This research represent a significant advancement in the development of “smart” materials finishes for garments and equipment.

**COLL 114**

**Spatial frequency heterodyne imaging of water filled multiwalled carbon nanotubes**
Evaporation and condensation of water on multi-walled carbon nanotube (MWCNT) surfaces was monitored as a function of both temperature and time using x-ray Spatial Frequency Heterodyne Imaging (SFHI). SFHI is an imaging method that produces an absorption and scatter image from a single exposure, with increased sensitivity to variations in electron density relative to more common place x-ray imaging techniques. Different features seen in the temporal scatter intensity profiles recorded during evaporation and condensation revealed the existence of an absorption-desorption hysteresis. Effects on the previously mentioned phenomena due to chemical functionalization of the carbon nanotube surfaces were also observed. Functionalization increased the interaction potential between the MWCNT walls and water molecules, altering the evaporation event time scale and increasing the temperature at which condensation could take place. The observed temperature dependent changes in evaporation time scales coincide with the boiling point for confined water predicted by the Kelvin equation.

**COLL 115**

**Triblock microparticles at fluid-fluid interfaces**

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In this work, we present the interactions and self-assembly of triblock microparticles at fluid–fluid interfaces. ABA-type triblock microparticles with different block ratios and surface wettabilities are prepared using a micromolding method. These triblock microparticles at fluid–fluid interfaces induce complex interface deformation depending upon their relative block ratio and the surface wettability. It is observed that triblock microparticles generate octapolar interface deformation at the air–water interface, whereas the same particles cause quadrupolar deformation at the oil–water interface. Consequently, the interactions and assembly behavior of these triblock microparticles at each fluid interface strongly depend upon the nature of the interface deformation.

**COLL 116**

**Self-assembled monolayers of amphiphilic macromolecules as bioactive cardiovascular stent coatings**
Each year, over 500,000 stents are implanted to provide mechanical support and regain adequate circulatory flow in atherosclerotic vessels occluded by lipid-laden plaque. Drug-eluting stents release cytotoxic or immunosuppressive drugs that minimize smooth muscle cell (SMC) proliferation, which can lead to blood vessel reocclusion. However, increasing evidence suggests that drug-eluting stents have similar mortality rates to uncoated bare-metal stents due to the delayed healing, inflammation, and hypersensitive reactions associated with drug and polymer coatings. Recently, amphiphilic macromolecules (AMs) comprised of a sugar-based hydrophobic domain and a hydrophilic linear poly(ethylene glycol) tail were found to be non-cytotoxic and suppress smooth muscle cell proliferation. In this study, we developed a self-assembled coating designed to gradually release bioactive AMs from metal surfaces. Carboxyl- and phosphonate-terminated AMs were grafted on stainless steel substrates using a grafting-to approach to evaluate the effect of either head group on bioactive loading and release. The chemical composition, thickness, grafting density, and wettability were quantified by X-ray photon spectroscopy, ellipsometry, contact angle, and diffuse reflectance infrared Fourier transform methods. Additionally, in vitro bioactive release was investigated by quartz crystal microbalance and coated substrates were evaluated in an SMC proliferation assay. These studies demonstrate that AMs assembled on stainless steel release in a controlled manner and suppress SMC proliferation, demonstrating the potential of using AM self-assembled monolayers as bioactive agents for sustained delivery from coronary stents and other metal-based implants.

COLL 117

Molecular simulations of phospholipid self-assembly: Curvature and nanoscale forces in vesicles and upon substrate adhesion

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The self-assembled form of a lipid aggregate in aqueous solution contributes to, e.g., dispersion efficiency, functionality in drug transport, and many crucial biological processes like motility, fission, fusion and trafficking. At a molecular scale, the self-assembled structure in aqueous solution is coupled to molecular spontaneous curvature. An interface imposes an external constraint, which influences the assembled morphology. Here, we have studied the coupling between molecular spontaneous curvature and the imposed external curvature in self-assembling lipid systems via molecular simulations.

We have mapped the adsorption morphologies for lipids of varying curvature as a function of substrate and lipid characteristics; the external curvature imposed by the
substrate acts as a control factor in determining the morphology [1]. This can be exploited in size-selective dispersion of hydrophobic nanoscale objects [2] or in design of more effective antimicrobial films through improved understanding of carbon nanotube dispersion in the system [3]. Here we show the introduction of external curvature can result in entropy driven phase separation in two-component lipid systems. The behavior differs vastly from liposomes in which the stresses from spontaneous molecular curvature can be relaxed between leaflets. We compare and connect our findings with theoretical considerations and experimental work on lipid adhesion and adsorption morphologies.


COLL 118

Fabrication of single neural cell chip to analyze cellular redox state by spectroelectrochemical technique

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Various kinds of in vitro cell based research were focused on examining the effect of treated materials (chemicals, anti-cancer drugs, various kinds of nanoparticles) on the target cells. In this case, examining local state of target cell is very important. But exact analysis of target cell state is difficult because of the complexity of living cells. Here, we introduce the single cell chip to analyze cellular redox state by spectroelectrochemical technique which combined with surface enhanced Raman scattering (SERS) and linear sweep voltammetry (LSV).

In this study, we fabricated polystyrene (PS) assisted nanopatterned between microgap electrode surface. PS particles with 100nm diameter were spin coated on cleaned microgap electrode then, pure gold was coated by thermal evaporation method with 30nm thickness to fabricate gold nanodot array between pairs of gold microelectrode. After gold nanodot array patterned microgap electrode fabrication, single PC12 cell was seeded on microgap between pairs of gold microelectrode. After PC12 cell immobilization, spectroelectrochemical measurement was done. During the oxidation
and reduction process of PC12 by LSV, Raman spectrum was changed relative to the control single PC12 cell. Mainly changed things in Raman spectrum during redox process is around 1560cm⁻¹. Compare with spectroelectrochemical analysis from dopamine, single PC12 cell shows similar response. Due to PC12’s secreted dopamine peak was involved in the redox process.

Our newly developed single cell analysis method can be apply to in situ label-free monitoring tool for biochemical composition changes in single cell by spectroelectrochemical analysis.

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**References**

**COLL 119**

**Bridging the pressure and materials gap between surface science and catalysis: Probing the surface of metal oxide nanoparticles**

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The surface chemistry of catalysts is important, but classically surface science is studied under ultra-high vacuum conditions while catalysis occurs under ambient conditions. Therefore, a pressure gap exists between these two different fields of study. Furthermore, a materials gap exists in which traditional surface science uses well defined crystal planes in order to study the surface reactions whereas application based fields such as catalysis employ more complex systems composed of several crystal planes. Metal oxide semiconductor particles are used in catalysis and contain a complex matrix of crystal planes, metal/oxygen bonds, metal/hydroxyl bonds, and oxide/water interactions. The surface of metal oxide semiconductor particles is rather difficult to study under ambient conditions. Bridging the pressure and materials gaps between classical surface science study and heterogeneous catalysis requires a different experimental approach. Transmission infrared spectroscopy is used to monitor reactions between gaseous adsorbates at different pressures (ambient to high vacuum), such as formic acid, acetic acid, and water, and metal oxide particles, ZnO and ZrO₂, which are widely used catalytic substrates. Additionally, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is used to analyze product formation on the surface of these semiconductor powders after exposure to gases. Spectral shifts in frequency, peak area and width values, and absorbance values are used to interpret the structure and reactivity of the semiconductor surface.
COLL 120

Preparation of large-area graphenes via mild oxidation followed by millstone exfoliation

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Mild oxidation of graphites was carried out by modified Hummers method at 20 °C for 15 to 60 min with reduced amount of KMnO₄ and termination with large amount of DIW. The mild oxidized graphite solutions (1mg/ml) were left overnight, and then decanting top water and adding same amount of DIW. This process, so-called DIW washing, was repeated twice to remove salts as well as acid. Next, the oxidized graphites in solution were grafted with aryl diazonium salts (1mg/mg) and then exfoliated with home-made millstone of glass plates. The graphite solution was milled 5, 10, 15 or 20 times and after each run, solutions were analyzed by UV-vis absorption as well as SEM. Finally, the solutions were centrifuged to isolate graphenes and analyzed by TEM, AFM and Raman. In addition, sheet resistance was measured and graphene yield was estimated.

COLL 121

Design and evaluation of ligand-conjugated amphiphilic macromolecule nanoparticles for mitigation of atherosclerosis

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Cardiovascular disease (CVD) begins with atherosclerosis, in which oxidized low-density lipoprotein (oxLDL) is uncontrollably internalized by macrophages, leading to foam cell formation, fatty streaks, and arterial plaques. We have previously designed amphiphilic macromolecules (AMs), comprised of an acylated sugar backbone and poly(ethylene glycol) (PEG), that significantly reduce oxLDL uptake by competitively binding to scavenger receptors (SRs). AM nanoparticles (NPs), with a core/shell design, exhibit improved efficacy in mitigating atherosclerotic progression, but do not influence disease regression. Natural agonists for the Liver X Receptor (LXR), a transcription factor for cholesterol efflux protein ABCA1, were incorporated into AMs to reduce the lipid laden foam cell phenotype. To enable NP shell formation, ligands were PEGylated or strategically conjugated to existing AMs for enhanced functional group presentation in the LXR binding pocket. Additionally, LXR ligands were modified to enable NP core encapsulation to increase bioactive loading. Ligand-conjugated AMs and cores were formulated into NPs with different core/shell combinations to assess their ability to inhibit atherosclerotic progression and reduce the lipid burden associated with later disease stages. Influences on markers indicative of atherosclerotic progression were evaluated, including oxLDL uptake and SR expression. Atherosclerotic regression
markers such as ABCA1 gene expression and foam cell phenotype were also assessed. Collectively, ligand-conjugated AM NPs offer a novel technology with the potential to both minimize atherogenesis and reverse lipid burden to reduce the prevalence of CVD.

Co-engineering the supramolecular nanoparticle-protein interface

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Tuning the molecular recognition between proteins and nanoparticles (NPs) is of fundamental importance in therapeutic applications and sensor development. Considerable effort has been directed towards optimization of nanoparticles for effective interaction, however there has been far less exploration in terms of engineering of the protein partner. Here we report a strategy to enhance the affinity and selectivity of NP-protein interaction by co-engineering of both particle and protein. We will discuss effective strategies for generating robust NP-protein dyads.
Supramolecular interaction between NPs and protein

**COLL 123**

**Structured surfaces for adhesion and friction experiments**

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Structured surfaces were prepared by adsorption of gold nanoparticles and polymer films on flat substrates. The polymer surfaces with different roughness and chemical heterogeneity were prepared by self-assembly of block co-polymers and by soft lithography replication techniques. Their structure, adhesion, and friction were investigated by atomic force microscopy (AFM) and their suitability as substrates in friction measurements with the Surface Forces Apparatus (SFA) technique was evaluated in preliminary experiments.

**COLL 124**

**Robust network microcapsules with tunable permeability based on sole cellulose nanocrystals**

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We have successfully fabricated robust “open-shell” microcapsules from sole biocompatible and biodegradable abundant natural cellulose nanocrystals (CNC) via LbL self-assembly. In strike contrast to the usually exploited microcapsules composed of traditional polyelectrolytes, the unique robust nanorod-like morphology of cellulose nanocrystal enables extreme porosity thin shell structure. Instead of encapsulation of macromolecules, the CNC microcapsules can be utilized for encapsulation of latex.
beads with a diameter from tens of nanometer to hundreds nanometer. The porous shell morphology and loading/unloading behavior were controlled with varying the number of assembled layers, deposition conditions and external pHs. Furthermore, the outstanding Young’s modulus of cellulose nanocrystals contributes to the remarkable robust mechanical property of the microcapsules as measured by AFM nanomechanical studies. The unique permeability and robust CNC thin shell present a promising platform for stable and tunable microcontainers for encapsulation and delivery of nanoparticles, cells and potential applications in biosensing.

**COLL 125**

**Nonlinear optical probe of chemical reactions and photonics at the surface of silver nanoparticles**

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Nonlinear light scattering, such as Second Harmonic Scattering (SHS), has been applied to probe the adsorption and reactions of thiol molecules at the surface of silver nanoparticles (40 nm radius). The activation energy, free energy change, and adsorption density of the reactions of a variety of neutral and anionic thiols at the particle surface have been measured. The reaction mechanisms at the molecular level have been deduced. The neutral vs charged thiols have qualitatively different reaction mechanisms that reflect the effect of charge-charge interactions at the surface. It is also found that adsorption of thiols may anneal the surface defects that quench photoexcitation, and subsequently enhance the luminescence efficiency of silver nanoparticles. The luminescence efficiency can increase by as much as 300 times through thiol modification of the particle surface.

**COLL 126**

**Nanomechanical properties of eutectic gallium-indium particles by atomic force microscopy**

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Eutectic Gallium-Indium (EGaIn) alloy is a liquid metal at room temperature that, under air, forms a passivating native thin (~0.7 nm) oxide layer. This oxide layer plays an important role in the overall mechanical properties of the alloy. The metallic and physical properties of EGaIn make it effective at conducting, and dissipating, heat away from temperature sensitive components. Being a deformable liquid metal, EGaIn is
consistently electrically conductive even when a supporting polymeric channel is excessively stretched. EGaIn particles, with a liquid core and a thin oxide shell, are created with diameters that range from 6.4 nm to >10 μm using fluidic shearing. The mechanical properties, such as the flexibility of the oxide shell, especially on nano- and micro-particles, are unknown. Atomic Force Microscopy, however, is a versatile instrument for imaging surface topography as well as for characterizing material properties, such as elasticity and film thickness at the micro- and nanoscale via force-distance curves (F-D curves). F-D curves are the result of interactions, upon contact, between an AFM tip and the surface of the sample due to the elastic force of the cantilever and values can be measured with resolutions up to pico-Newton. This poster describes our studies on surface tribology of EGaIn particles of various sizes via AFM F-D curves.

COLL 127

Kinetic release of micellized PEG-PLL block copolymer complexed with siRNA using FRET assay

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Efficient and effective therapeutic agent delivery to specified sites in the body is a goal for investigators in order to achieve better drug performance. However, challenges arise to assembling the delivery vehicle since most therapeutics cannot exist in the body and transported without aid and previous agents, such as viral vectors, are limited due to their safety factors. In this study, the specific therapeutic of interest is siRNA, which contains 21 base pairs and is negatively charged. These characteristics and its hydrophilicity make naked siRNA non-ideal for its isolated transportation, but ideal for complexing with a cationic block copolymer. Block copolymers have previously been studied as a vehicle for drug delivery with promising results. Here, we take a kinetic approach for a mechanistic understanding of the micellized particle disassembly. To achieve effective delivery, the component must remain intact while outside a cell and be able to disassemble once inside. Understanding this release is crucial for ensuring proper gene delivery. In this study, two siRNA duplexes were labelled with Alexa Flour fluorescent probes. These were then allowed to micellize with cationic poly-L-lysine (PLL), leaving nonionic poly(ethylene glycol) (PEG) as the more outer layer of the micelle. Block copolymer PEG-PLL with 50 PLL units was chosen for this study, because of its favorable characteristics. PLL has been a common cationic polymer used for delivering agents such as siRNA, it has been shown to improve transfection efficiency, and reduce toxicity. 50 units of PLL has been shown to be the most stable length for use as a delivery agent. PEG is often added to biomaterials for increased biocompatibility, improved solubility, and to reduce cell toxicity. When the duplexes were together they emitted a Förster resonance energy transfer (FRET) signal. Thus, when siRNA probes were encapsulated within the micelle, the
FRET signal was “on,” and when the particle would disassemble, the FRET signal dampened. Using a microplate assay, this FRET signal could be monitored over a period of time, and a reading could be generated with excitation at 540 nm and emission at 620 nm. Initial experiments were performed in physiological relevant medias, such as 10% FBS and glutathione (10mM). Ultimately, this work has significance in quantifying the release of siRNA from a promising block copolymer vehicle candidate using a FRET assay.

**COLL 128**

**Photoreactive sulfobetaine copolymers for the modification of biomedical devices**

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Zwitterionic betaine polymers, such as those containing sulfobetaine, are suitable for use as films for biomedical devices. They have been shown to reduce the adhesion of microorganisms to the surface of the device in question, significantly cutting down on the risk of infection as well as thrombosis. Betaine polymer brushes have been grafted-from substrates through surface-initiated polymerization to achieve the best anti-fouling performance and in vivo stability. This study investigates photo-reactive copolymers that can effectively generate a similar anti-fouling layer on medical devices. A series of copolymers featuring sulfobetaine methacrylate (SBMA) and various methacrylate benzophenone monomers is described. The photoreactivity of benzophenone is exploited in order to covalently attach the copolymer to the surface of various substrates including polyvinyl chloride and polyurethane. The copolymers are designed to form a hydration layer with highly bound water, equivalent to polymer brushes after being applied on substrates and activated by UV light. This method is utilized with the goal of attaching SBMA copolymers to the surface of biomedical devices including endotracheal tubes and venous catheters. Efficacies of the coatings were tested using radioactive mucin and fibrinogen assays, showing high reductions in attachment for treated samples. Results were comparable with previously studied graft-from chemistries for sulfobetaine modification.

**COLL 129**

**Characterization and antibacterial effect of silica-silver nanocomposite particles**

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The chemistry of hybrid silica materials remains as an actively investigated theme because of its relevance to various fields such as applications in adsorbents, optical devices, and catalysts. In this experiment, surface of silica particles is modified with 3-Mercaptopropyltrimethoxysilane (MPTMS). Silver particles (NPs) is chemically binded on silica surface to form silica-silver nanocomposite particles (NCPs). The silica-silver...
NCPs were synthesized within two steps and were characterized by UV−vis spectroscopy, Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), and X-Ray Diffraction (XRD). Silver is well-known as an antibacterial material which can effectively block fungi or viruses. In this experiment, 3 samples have been prepared: polymer film without coating, polymer film with silver NPs coating and polymer film coated with silica-silver NCPs. The antimicrobial ability and stability of the material will be further determined by varying reaction temperature and time.

COLL 130

Cytosolic delivery of therapeutic siRNA and miRNA using self-assembled gold nanoparticle-stabilized nanocapsules for breast cancer therapy

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siRNA and miRNA based therapies have great promise for treating cancer. There are two key challenges for the use of siRNA and miRNA as cancer therapeutics. The first challenge is effective delivery into the cell. An even greater challenge, however, is access to the cytosol, as almost all carrier-based delivery strategies proceed through endosomal pathways. As a result, most current delivery vehicles are too toxic or inefficient to be used in a cancer therapy. We have developed non-toxic gold nanoparticle-stabilized nanocapsule (NPSC) delivery vehicles to deliver short RNA therapeutics targeted against proteins that promote breast cancer. The nanocapsule delivery vehicle consists of cationic arginine-functionalized gold nanoparticles that are complexed with negatively charged siRNA or miRNA molecules. These complexes self-assemble on emulsified oil cores to generate ~120 nm NPSCs. These NPSCs deliver the siRNA/miRNA cargo directly into the cytosol through a membrane fusion mechanism that avoids endosomal entrapment and allows for functional cytosolic delivery of siRNA/miRNA. We have demonstrated effective knockdown of protein, and have used RT-PCR results to confirm the decrease of mRNA transcripts after delivery of correct sequence siRNA. Cell viability and migratory assays confirm the therapeutic effect of the specific protein knockdown on breast cancer cells. NPSC delivery efficiency is markedly superior to commercial transfection reagents, showing the therapeutic potential of NPSCs.

COLL 131

Triethanolamine-stabilized silver nanoparticles as substrates for surface-enhanced Raman scattering
A facile method for the preparation of water soluble silver nanoparticles (Ag NPs), using triethanolamine (TEA) as both a reducing agent and a particle stabilizer is reported. The synthesis was studied via changes in reaction temperature, pH, and Ag:TEA ratio. The most promising samples were highly stable, relatively monodisperse (particles ca. 20 nm in diameter), and displayed a strong localized surface plasmon resonance (LSPR) around 410 nm. These samples were employed as substrates for surface-enhanced Raman scattering (SERS) of rhodamine 6G and thiosalicylic acid. SERS measurements were conducted using laser excitation at 514 and 830 nm, and the Ag nanoparticles were found to provide significant enhancement of the Raman scattering of these test analytes.

COLL 132

Characterization of hybrid microspheres with silica nanoparticles-embedded surface

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Microspherical core-shell particles have been attracting much attention and are used in various industrial fields such as pharmaceutics, cosmetics electronics, photonics and separation science. Previously, we reported that the hybrid microspheres with silica nanoparticles-covered surface could be prepared by modified O/W suspension polymerization.¹) Assembled-structure of the silica nanoparticles at the interface of the polymerizable monomer (oil phase) and water as a suspension media could be tuned by controlling of hydrophilic-hydrophobic balance (HLB) of the surface of silica nanoparticle. 3-Methacryloxypropyltrimethoxysilane (MAPTS) was used as a surface modifier with polymerizable group. For example, silica nanoparticles with more hydrophobic surface are embedded deeply into polymer core whereas silica nanoparticles with more hydrophilic surface embedded shallowly into polymer core. The packing density of silica nanoparticles on the surface of core polymer could be controlled by changing the loading amount of silica nanoparticles. Interestingly, when relatively small amount of silica nanoparticles was used, a two-dimensional periodic non-close-packed array of silica nanoparticles was observed on the surface of polymer core (Fig. 1b). This is probably due to the electrostatic repulsion between the remaining silanol groups on the silica nanoparticles. On the other hand, relatively large amount of silica nanoparticles was used, waved-surface with densely-packed silica nanoparticles was observed (Fig. 1c). Their surface structure was controllable with HLB, loading amount and size of MAPTS-modified silica nanoparticles. The reflectance and water repellent properties of
microspherical core-shell particles with various surface morphologies were examined by UV-vis spectrophotometer with integrating sphere and contact angle meter respectively. The results indicated that the silica nanoparticles on the surface of polymer core was covered with polymer component and the surface morphology was effective to the reflection property.


Figure 1 SEM images of hybrid microspheres with silica nanoparticles-embedded surface with various amounts of silica nanoparticles.

**COLL 133**

**Correlating excitonic and structural properties of lead sulfide (PbS) nanocrystal films**

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Lead sulfide (PbS) nanocrystals have a size-dependent, tunable band gap in the infrared region, making them particularly interesting for photovoltaics, photodetectors, and infrared communication. In many of these applications it is necessary for excitons to diffuse long distances in the nanocrystal film as part of the injection (in LEDs) or extraction (in photovoltaics) process. However, the physical structure of these films can vary significantly as a function of the size dispersity of the nanocrystals and the processing conditions. In this work we correlate the structural properties of PbS nanocrystal films (amorphous vs. ordered, dipole aligned vs. random dipole orientation) with their exciton transport properties. To study this relationship, we have carefully varied the size dispersity of our materials as well as their surface ligand coverage to access varying degrees of both energetic dispersity and structural ordering. We have characterized the physical structure of our thin films using grazing-incidence small-angle X-ray scattering (GISAXS) and high resolution scanning electron microscopy (SEM). The optical properties of the films were studied using a combination of spectrally-
resolved time-correlated single-photon counting and time-resolved optical microscopy to visualize exciton diffusion.

High resolution scanning electron micrographs of PbS nanocrystal superlattices

Time-correlated spectrally-resolved photoluminescence emission from a PbS film showing a redshift in the emission as a function of time, indicating exciton diffusion

**COLL 134**

Comparative study on the single particle optical properties of binary CdSe and ternary alloyed CdSₙSe₁₋ₙ semiconductor nanocrystals

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Ternary alloyed (AB\textsubscript{x}C\textsubscript{1-x}) semiconductor nanocrystals (NCs) are recently emerging as an important class of materials with its potentials in areas of nanoscale engineering due to the continuous tunability of their optoelectronic properties through gradual variation of their composition. This added degree of freedom allows fine tuning of the energy bandgap of these materials independent of the overall nanocrystal volume which can be used to extend their emission over a wide spectral range (UV-near IR) that are often not accessible with the regular binary quantum dots (QDs). Here, in this work, we have synthesized various alkylamine capped CdSSe QDs at a comparatively lower temperature than most of the earlier reported hot injection synthetic approaches. The structural and elemental analysis of the synthesized nanocrystals was carried out by transmission electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy. The photoluminescence (PL) properties, such as lifetimes and emission intensity time traces of single QDs were investigated. From the PL time traces, the distributions for “on” and “off” events of these single QDs were analyzed and compared with that of the conventional CdSe QDs of similar size and emission range. We observed that these alloyed QDs were more photostable compared to their binary counterparts. This may be due to more efficient surface passivation and a rather core/shell like structure resulting due to the reactivity differences in the anionic precursors. So, in certain specific applications like in-vivo imaging and multiplexing where size plays a more essential role, these kind of ternary alloyed QDs can act as preferable candidates over conventional binary QDs.

**COLL 135**

**Synthesis and stabilization of CuO nanorods in alkane based solvents**

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**Abstract:** Incorporation of nanometer-sized particles in various liquids, including phase change materials (PCM), is a possible way to achieve enhanced thermal properties beyond Maxwell predictions. Of particular interests are PCM systems in which thermal transport is accelerated by the particles, also known as nanostructure enhanced phase change materials (NePCM). Spherical metal or metal oxide particles were prepared previously in various alkane based solvents and showed little influence in the overall thermal conductivity although a very high concentration of metal particles were achieved (1.0 M). Rod-like particles were hypothesized to induce a higher enhancement of thermal transport as compared to spheres. CuO rods with a yield of \( \approx 100\% \) were successfully synthesized in aqueous medium and stabilized for at least a month in organic solvent such as octane and tetradecane. UV-Visible spectral measurements on the stability of rods, as well as transmission electron microscopic (TEM) and XRD results of the CuO rods will be presented. The resultant CuO rods transform into spherical Cu particles after reduction in alkane.

**COLL 136**
Reactive fibrous adsorbents for decontamination of chemical threats

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In addition to ongoing concerns about chemical warfare agents (CWAs), there is also a growing need for decontamination of industrial chemicals as well as acetylcholinesterase-inhibiting pesticides, among others. Thus, it is imperative to effectively detoxify a broad spectrum of toxic agents, including, but not limited to, organophosphorus-type compounds, from contaminated surfaces and sensitive equipment. The objective of immediate decontamination operations is to remove toxic agents from the contaminated surface as rapidly as possible. However, traditional adsorbents, while effective at removing chemical agents, do not possess sufficient reactive properties to neutralize the sorbed toxic agents and thus, become a threat from off-gassing toxins and/or sorbed vapors. Our work focuses on development of novel polymeric reactive sorbents that both sorb and react with CWAs and their simulants to yield less toxic products. In this work, we introduced a concept of polymeric amines that possess enhanced nucleophilicity and hence, ability to catalyze hydrolysis of organophosphates as well as degradation of sulfur mustard agents. Polymers such as polyalkylamines modified with 4-aminopyridine, poly(butadiene-co-pyrrolidinopyridine), poly(N,N-diallylaminopyridine-co-vinylamine-co-vinylformamide) are capable of augmenting the rate of hydrolysis of CWA and their mimic diisopropylfluorophosphate (DFP) many-fold. These polymers also cause rapid dehydrochlorination of sulfur mustard and its analogue 2-chloroethyl ethylsulfide (CEES). We describe technologies of covalent attachment of supernucleophilic polymers to fibrous materials such as rayon and Kevlar fibers using multifunctional isocyanates. The fibers are characterized by various microscopy and spectroscopic techniques as well as examined for their reactivity toward DFP in the presence of moisture and by dynamic vapor sorption of CWA simulants. Mechanistic aspects of decontamination using fibrous nucleophilic materials as well as their utilization in protective fabrics are discussed.

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COLL 137

Advances in the use of gel permeation chromatography (GPC) to nanocrystals: Purification, solvent change, and surface modification

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Gel permeation chromatography (GPC) has been established in our lab as a method to purify semiconductor nanocrystals (NCs), and we believe that well-isolated and
characterized nanomaterials are essential to build up sequential chemical method in nanoscience. In this presentation, I will describe some of our most recent works using GPC purified semiconductor nanoparticles: (1) to study the photo-physical properties associated with the interfacial ligand chemistry: we characterize changes in ensemble quantum yield (QY) and lifetime components on introduction of neutral ligands to purified NC samples; (2) to perform surface modification reactions with GPC purified quantum dots: a range of polymeric imidazole ligands prepared by RAFT polymerization and post-modification were synthesized and associated to NC surface to provide water solubility, colloidal stability and high brightness; (3) to use GPC as a reactor to perform solvent change and ligand exchange reactions with variety of NCs.

COLL 138

Adaptation of FTIR spectrometer to the external reaction chambers for surface analysis studies

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Infrared spectroscopy is well known technique to probe chemistry at the surfaces down to monolayer thickness. Surface modifications are carried out in reaction chambers either in ultra-high vacuum (UHV) or under gas flowing above the sample. Adaptation of reaction chamber to FTIR spectrometer is required in most cases because reaction chambers are bulky. In typical setup IR beam is focused to the sample mounted in the external chamber and external detector collects IR light from the sample. There are many technical difficulties that might be solved in designing such adaptations: beam divergence, matching beam size in focus and sample size, enclosing beam path, selecting windows, flanges, etc. Optimization of external setup will be discussed in this presentation. This will include:
-introducing intermediate IR beam focus to fit beam to elongated reaction chamber
-using slit aperture to maximize signal
- IR beam expansion that will allow to bring beam to the distant chamber
Several customized adaptations for reflectance and transmittance measurements in the same reaction chamber were developed. Their design and features will be presented.

COLL 139

Atomically precise gold nanoclusters for the electrocatalytic reduction of carbon dioxide

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Many technological approaches have been explored to reduce CO\textsubscript{2} emission to the atmosphere. Of the diverse approaches of CO\textsubscript{2} conversion, electrocatalytic conversion
of CO\textsubscript{2} to valuable chemicals such as syngas, CO, formic acid, and methanol has received much attention recently. However, the electrode materials such as Cu and Ag currently employed in the electrocatalytic reduction of CO\textsubscript{2} exhibit large overpotential and low current density, which makes it difficult to develop carbon neutral process from electrocatalytic methods. In this poster, we report that atomically precise metal nanoclusters for example, Au\textsubscript{25}(SR)\textsubscript{18} where SR is thiolate, can be effectively used as homogeneous and heterogeneous catalysts. CO\textsubscript{2} reduction potential was found to be -1.6 V vs. NHE at a glassy carbon electrode in CH\textsubscript{2}Cl\textsubscript{2}, which decreased significantly in the presence of Au\textsubscript{25} nanoclusters. The metal nanoclusters offer special advantages in the development of electrocatalysts. Various types of nanoclusters can be prepared by doping nanoclusters with foreign metals such as Pt, Pd, Cu and Ag. The preparation and effect of doping in the electrocatalytic reduction reaction are presented. Au\textsubscript{25}-based modified electrodes were also found to be an efficient heterogeneous catalyst for the reduction of CO\textsubscript{2}. The electroreduction of CO\textsubscript{2} was found to start at -1.2V at glassy carbon electrode in aqueous media and to drastically shift positively at the modified electrode coated with Au\textsubscript{25}-based nanoclusters.

**COLL 140**

**Modified electrodes using Au\textsubscript{25} nanoclusters for electrochemical sensing applications**

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Recently thiolate protected Au\textsubscript{25} nanoclusters (NCs) have attracted much research interest due to their unique electrochemical and optical properties. Previous studies revealed that Au\textsubscript{25} NCs showed excellent electrocatalytic activity toward the oxidation of dopamine, ascorbic acid and uric acid. Au\textsubscript{25} NCs with these electrochemical properties can be utilized in a variety of electrochemical applications. In this study, we examined several matrices for the immobilization of Au\textsubscript{25} NCs on electrodes. Sol-gel technology has been commonly used for the encapsulation of a variety of materials including gold nanoparticles. Au\textsubscript{25} NCs were immobilized into (3-mercaptopropyl)-trimethoxysilane (MPTMOS) network via thiol linkers to form Au\textsubscript{25} sol-gel electrode (Au\textsubscript{25}SGE). Cyclic voltammograms of Au\textsubscript{25}SGE exhibited stable, well-defined and reversible redox peaks of Au\textsubscript{25} NCs. In addition, enzyme sol-gel electrodes prepared by immobilizing glucose oxidase (GO\textsubscript{x}) on Au\textsubscript{25}SGE showed electrocatalytic activity toward the oxidation of glucose. In another study, we explored the possibility of using cationic polymers, for example chitosan and polyethyleneimine (PEI), to immobilize Au\textsubscript{25} NCs. Whereas the redox peaks of Au\textsubscript{25} NCs in chitosan were not well-resolved, they became clearly resolved by the addition of an ionic liquid, for example 1-decyl-3-methylimidazolium tetrafluoroborate (DMImBF\textsubscript{4}). In addition, the modified electrodes by immobilizing Au\textsubscript{25} NCs in PEI exhibited electrocatalytic activity toward the oxidation of ascorbic acid. The electrochemical sensing properties of Au\textsubscript{25} NCs immobilized in these matrices are also presented.
Iron chalcogenide nanoparticle precursors for solution processed photovoltaics and other applications

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Sustainable, low-cost materials such as FeS$_2$ could address environmental and economic concerns raised by amorphous-Si, CdTe and CIGS in thin-film PV. However, to date, FeS$_2$-based devices show low efficiencies (~ 2%). Alternatively, Fe$_2$SiS$_4$ and Fe$_2$GeS$_4$ could circumvent these limitations. With an estimated direct bandgap of ~1.55 and ~1.4 eV for Fe$_2$SiS$_4$ and Fe$_2$GeS$_4$ respectively, and an absorption coefficient $>10^5$ cm$^{-1}$, the two ternary materials that are subject of our research hold theoretical solar cell efficiency potential comparable with current materials (>20%) and can operate at a 0.1μm required thickness to accomplish similar performance with other thin film materials (such as CIGS)$^1$.

We focus on a nano-scale approach to Fe$_2$SiS$_4$ and Fe$_2$GeS$_4$ absorber layers toward fabricating high-efficiency solar devices. The nanoparticles synthesis, purification, deposition and conversion in polycrystalline films will be presented.

The sustainable, inexpensive Fe$_2$SiS$_4$ and Fe$_2$GeS$_4$ materials along with the solution-processing methodology could reduce installation costs by enabling use of light-weight, flexible substrates and thus align with the needs of cost reduction in PV.


Photocatalytic performance of a trifold nanocomposite material for the hydrolysis of 2-chloroethyl ethyl sulfide (CEES)

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Chemical warfare agents (CWAs), classified as weapons of mass destruction, pose a constant threat to warfighters and civilians worldwide. CWA contaminated environments have been known to cause serious health hazards to exposed human beings, including damage to the nervous system, respiratory collapse, convulsions, and even death. Previous and ongoing research has been done towards the efficient detection and degradation of CWAs. Photocatalysis, the acceleration of a chemical reaction by light in the presence of a catalyst, has been found to be an emerging area for the rapid degradation of various CWAs and simulants. A trifold nanocomposite material
composed of tungsten oxide nanoparticles coated onto poly(4-vinylpyridine) single walled carbon nanotube (WO3-PVP-SWNT) was synthesized and its photocatalytic performance for the hydrolysis of 2-chloroethyl ethylsulfide (CEES), a mustard gas simulant, was studied by NMR spectroscopy. The photocatalytic performance of WO3-PVP-SWNT has been compared to those of its two precursor compounds, WO3 nanoparticles and poly(4-vinylpyridine) single walled carbon nanotube (PVP-SWNT), as a means of examining whether the presence of both WO3 and PVP-SWNT will synergistically contribute to a faster rate of conversion. Each kinetics test consisted of preparing a solution of CEES (20 mL) in 50% water/50% acetone-d6, adding it to ~2 – 3 mg of the solid material. The 1H NMR spectrum was measured prior to irradiation and the solution was irradiated for a total period of 30 minutes, measuring the NMR spectrum at various irradiation intervals. Kinetics measurements were taken at the CEES triplet peak at d 2.8 ppm. The first order rate constants (k) for the hydrolysis reaction were found to be 0.00087 s⁻¹ (presence of WO3-PVP-SWNT) and both 0.00064 s⁻¹ (in the presence of PVP-SWNT and WO3 alone). The NMR results show that WO3-PVP-SWNT exhibits a slightly better photocatalytic performance than individual PVP-SWNT and WO3, but not to a significant degree. Furthermore, the structural identity of the hydrolyzed product, 2-hydroxyethyl ethylsulfide (HEES), was determined from the NMR spectra.

COLL 143

Silver seeds and aromatic surfactants facilitate the growth of anisotropic metal nanoparticles: Gold triangular nanoprisms and ultrathin nanowires

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Here, we report that the introduction of silver seeds can lead to fast and high-yield syntheses of two highly anisotropic metal nanoparticles: triangular gold nanoprisms and ultrathin metal nanowires. Uniform sub-50 nm gold triangular nanoprisms were formed in high yields when silver seeds were introduced to the growth solution containing a small amount of silver ions and an aromatic surfactant, benzyltrimethyl hexadecylammonium chloride. On the other hand, gold seeds grew into spherical particles under the same condition. The formation of gold triangular nanoprisms from silver seeds was attributed to a relatively more reactive nature of silver seeds, which allows for the necessary structure evolution at the initial stage of nanoparticle growth. At high silver ion concentrations, ultrathin nanowires with the diameter of 1.6 nm were formed in nearly 100% yield. While both seeds (gold and silver) produced the same type of nanowires, silver seeds significantly facilitated the formation of nanowires, and the nanowire growth was almost instantaneous with silver seeds. We believe that the use of silver seeds in combination with aromatic surfactants can open up new possibilities for shape control of metal nanoparticles.
Synthesis of metal sulfide nanoparticles in toluene at room temperature

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Due to their unique optical and semiconducting properties, metal sulfide nanoparticles are excellent candidate materials for photovoltaic, catalytic, labeling, and sensing applications. In this work, small (1-10 nm) metal sulfide (Ag$_2$S, PdS, or CdS) nanoparticles were synthesized in toluene at room temperature. Tetraoctylammonium metal complexes of Ag, Pd, or Cd were first prepared and characterized. These complexes were then dissolved in toluene, and aqueous solutions of Na$_2$S were added, forming biphasic mixtures. Upon phase transfer of the sulfide ion, relatively monodisperse metal sulfide nanoparticles capped with tetraoctylammonium bromide were generated in the toluene phases. In some cases, 1-dodecanethiol was added as an additional stabilizing ligand. UV-visible absorption, fluorescence emission, infrared absorption, and Raman scattering spectroscopies, as well as X-ray diffraction and transmission electron microscopy were used to characterize the synthesized metal sulfide nanoparticles.

Quantifying the surface coverage of mercaptohexadecanoic acid on nanocrystalline SnO$_2$ thin films

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The surface coverage of mercaptohexadecanoic acid (MHDA) adsorbed on nanocrystalline SnO₂ thin films is presented. MHDA can act as a molecular linker in the attachment of quantum dots to the SnO₂ film, which would have applications in sensing and photovoltaic devices. SnO₂ thin films were prepared via a low cost doctor blade method, in which colloidal SnO₂ is spread across a glass substrate using a pastuer pipette. Nanocrystalline films were achieved with an annealing step at 450°C. SnO₂ films with an average thickness of 2 microns and an average particle size of 25 nm were characterized. Films were immersed in a 2 mM solution of MHDA in THF for at least 2 hours. Using FTIR spectroscopy, integrated absorbance was measured between 2800-3000 cm⁻¹. This region is where the CH₂ symmetric and asymmetric stretches occur from the surface adsorbed MHDA. Using a modified Beer-Lambert equation the surface coverage of MHDA on the SnO₂ film was calculated to be 1.1 ± 0.1 x 10⁻⁷ mol/cm², which closely agrees with previously reported surface coverages of MHDA on nanocrystalline TiO₂ thin films. Future studies will explore the catalytic nature of these SnO₂ films.

COLL 146

Single-phase synthesis of thiolate-protected metal nanoparticles

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A novel method for the single-phase synthesis of organosoluble thiolate-protected nanoparticles of several different metals (Au, Pd, Ag) is presented here. Ion-pair complexes of tetraoctylammonium cation and different metal-halide anions are reacted in toluene with an organosoluble reductant in the presence of alkanethiol. This facile, single-step reaction utilizes stable, well-defined precursor species and yields monodisperse nanoparticles comparable to those produced using multistep, two-phase methods.

COLL 147

Nisin protection from degradation and controlled release via polyacrylic acid encapsulation

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Biological agents are a threat to Soldiers and civilians. Many harmful bacteria, such as Staphylococcus Aureus and anthrax, are resistant to common antibiotics. There are bacteria that produce anti-microbial compounds known as bacteriocins. These target bacteria and perturb the cell membrane thus killing the bacterium. Bacteriocins have the potential to be used as a defense against specific bacterial agents; however there is a
challenge in maintaining their biological activity in a non-native environment. The goal of the work described here is to develop a method for bacteriocin encapsulation (using commercially available nisin as a model) that will protect it from degradation and prolong its release. This is done via polyelectrolyte complexation with polyacrylic acid (PAA) followed by crosslinking with methylenebisacrylamide (BIS). Polyelectrolyte complexes (PECs) are formed by electrostatic interactions between oppositely charged polymers. The charge ratio of the two polymers affects the size, stability, and surface charge of the PECs formed. When the ratio of one polymer to the other is great enough, full encapsulation is achieved. Nisin maintains a net positive charge and PAA maintains a net negative charge at pH 5. Thus, to form the PECs, each polyelectrolyte is dissolved in buffer at pH 5. The two solutions are combined in different ratios and the resulting particles are characterized via SEM, dynamic light scattering, and electrophoretic mobility. The particles are then crosslinked using BIS and evaluated for release kinetics. Finally, particles are aged and cultured with \textit{Staphylococcus aureus} to test bactericidal activity and to assess degradation prevention. This work lays a foundation to develop these techniques for other bacteriocins and for the future design of multifunctional textiles for the Soldier that incorporate targeted protection against biologics and provide greater overall defense against the elements.

**COLL 148**

\textbf{Versatile gold nanobowl arrays for size-selective plasmonic biosensing}

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Recent research in nanotechnology has shown that metal nanoparticle arrays, which exhibit localized surface plasmon resonance (LSPR) can be utilized towards biosensing applications. Unfortunately, selectivity and biofouling remain common drawbacks, since this type of biosensing requires biomolecules to bind directly to the nanoparticle surface. In order to add another layer of selectivity to our nanoparticle sensors, we have created gold nanobowl arrays which are capable of carrying out size-selective biosensing. Thus, when a molecule is small enough to fit into the nanobowl, the surface enhanced Raman spectroscopy (SERS) signal and LSPR shifts are increased when compared to a molecule that is too large to fit into the nanobowls. The gold nanobowl arrays were made through the galvanic ion exchange of a silver nanoparticle array produced using hole-mask colloidal lithography (HCL). The reaction was monitored using UV-Visible and NIR spectroscopy, and the structure width and shape were determined using field emission scanning electron microscope (FESEM) imaging. Experiments involving binding gold nanoparticles of different sizes indeed show increased SERS intensity and LSPR shifts for particles small enough to enter the interior of the nanobowls. In addition, the size-selective sensing of 95 nm H1N1 virus particles is achieved with 130 nm gold nanobowl arrays. These gold nanobowl arrays, showing increased biosensing selectivity can be useful and cost-effective for point-of-care medical diagnostics.

**COLL 149**
Directed self-assembly of nanoparticles: Template control of nanostructure configurations

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Self-assembly of colloidal nanoparticles offers a promising route to large-scale nanopatterning of particle superlattices at length scales inaccessible to conventional lithographic techniques. More complex structures can also be created through the use of directed self-assembly.\textsuperscript{1,2} However, even with the use of templates or other directing methods, there is still a trade-off between complexity and control of the resulting assembled structures especially at the nanoscale.

We studied the self-assembly of sub-10 nm gold nanoparticles (AuNPs) into 2D nanoarrays within a topographical template comprising lithographically-defined channels of varying width. AuNPs were drop-cast onto a silicon substrate patterned with hydrogen silsesquioxane resist (HSQ) lines, and the resulting assemblies analysed. Our experimental results supported by Monte Carlo simulations showed, despite the simplicity of the template, a structure transition\textsuperscript{3} through a rich variety of self-assembled configurations over a range of channel widths. In contrast to the packing of compressed hard spheres, the observed configurations frequently did not maximise the packing fraction. Instead there appeared to be a tendency for particles in the channels to stick to the sidewalls due to the effect of capillary forces in the assembly process.

Notably, the type of self-assembled configurations displayed by the particles was highly sensitive to the ratio of channel width to particle diameter. This suggests a possible approach for controlling the creation of complex nanostructures in a simple self-assembling system.

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This work was supported by the Agency for Science, Technology, and Research (A*STAR) in Singapore. The work made use of the SERC nano Fabrication, Processing, and Characterization (SnFPC) facilities in the Institute of Materials Research and Engineering (IMRE). Simulations were performed at the Singapore University of Technology and Design (SUTD).

Magneto-responsive hybrid colloidal architectures: Preparation, processing, and opal film formation

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Highly ordered three-dimensional colloidal crystal structures open access to various applications in the field of sensing, photonics, and membrane technology. The challenge is to exploit the benefits of ordinary opal structures making them smarter by the introduction of (chemical) functionalities which can be triggered by external stimuli. Besides common triggers, such as pH, solvents, temperature and salt concentration, especially fast and non-invasive stimuli, such as a magnetic field, are of high interest in regard to mentioned feasible applications. There are several routes known for the incorporation of magnetic components in sophisticated sensing devices. However, preparation routes often result in irregular magnetic particle alignments due to the presence of polydisperse ill-defined core/shell particles. Another major drawback of synthesis strategies is connected with an excessive effort in particle purification and processing. In this work, we present a synthesis strategy for the preparation of highly monodisperse magnetic nanoparticles using convenient emulsion polymerization protocols followed by a Stöber process. The introduction of 2-(methacryloyloxy)ethyl ferrocenecarboxylate (FcMA) in step-wise and one-pot emulsion polymerization followed by a convenient Stöber process opens access to highly functional stimuli-responsive particles. Subsequent thermal treatment opens access to magnetic hollow spheres with adjustable particle diameter due to adjustable synthesis protocols. Various magnetic hybrid particles can be obtained for the preparation of magnetically addressable opal films and double-inverse opals for novel sensing applications.
Synthesis and self-assembly of copper nanowires

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Single crystalline, one-dimensional nanostructures, such as nanotubes, nanorods, nanobelts and nanowires, exhibit unique catalytic, optical, thermal and electric properties that can be commercially exploited. Specifically, copper nanowires (Cu NWs) have found applications in printed circuit boards and as flexible and transparent electrodes for photovoltaic cells. Due to increasing demand for conductive nanomaterials in microelectronic industry, there is a need for rapid, bulk-scale and easily processable methods for CuNW synthesis. We present here a solution based and microwave assisted synthetic approaches for their large scale synthesis. Our method adopts a solution based synthesis approach\cite{1} to demonstrate controlled the aspect ratio of Cu NWs by varying the growth time period and the temperature of the reaction. A second method uses microwaves to assist in a rapid synthesis of copper nanowires \cite{2}. Here, we investigate feasibility of using lyotropic liquid crystalline (LC) media for alignment of nanowires at a micro and macroscopic level to improve their electrical conductivity. When dispersed in a solvent, above a particular concentration ($\phi_N$), rods or nanowires self-assemble to form a nematic liquid crystalline phase, where all nanowires or rods are orientationally ordered. Formation of such a ordered structures can be characterized by schlieren textures of disclinations under cross polarized optical microscope as well as scanning electron microscopy (SEM).

References:

COLL 152

Electron induced surface reactions of organometallic precursors

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Electron Beam Induced Deposition (EBID) is a resistless lithographic process which uses the electron stimulated decomposition of volatile organometallics under low vacuum conditions to fabricate three-dimensional metallic nanostructures. It has potential to become a robust tool for nanostructure fabrication if the deposit metal content can be improved. Towards this goal, the present study is aimed at understanding the surface-bound electron-stimulated reactions of two novel
organometallic precursors: η\(^3\)-allyl ruthenium tricarbonyl bromide \([\eta^3-C_3H_5]Ru(CO)_3Br\), and cis-dicarbonyldichloro platinum(II) \((\text{cis-PtCl}_2(\text{CO})_2\). X-ray Photoelectron Spectroscopy and Mass Spectrometry were used in situ to probe the effects of 500 eV electrons on nanometer scale films of both compounds. For \([\eta^3-C_3H_5]Ru(CO)_3Br\), electron irradiation initially decomposes the precursor, reducing the central Ru atom and causing ejection of CO ligands into the gas phase. In contrast, electron irradiation has minimal impact on the η\(^3\)-allyl ligand carbon atoms, which largely remain behind as contamination in resulting EBID deposits. Although the Br atoms are not labile in the initial molecular decomposition step, they are removed from the film under the influence of higher electron fluxes as a result of a slower electron stimulated desorption process. Comparative studies reveal that halogen identity does not influence the decomposition process. Similar behavior was observed during electron irradiation of cis-PtCl\(_2\)(CO)\(_2\): initial loss of the carbonyl ligands, followed by slower loss of the chloride atoms, resulting in nearly pure platinum films. These results are relevant to electron beam induced deposition (EBID), which uses much higher electron fluxes than our ultra-high vacuum (UHV) surface science experiments, and suggest that volatile organometallic precursors with a combination of carbonyl and halogen ligands could be used to create much purer EBID deposits (significantly higher metal contents and lower levels of organic contamination) than are currently possible with existing EBID precursors.

**COLL 153**

**Modification of nitinol nanoparticles with self-assembled monolayers**

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Nitinol nanoparticles, which are composed of fifty-percent nickel and fifty-percent titanium, are a valuable metal alloy due to shape memory, corrosion resistance, and superelasticity, making the nanoparticle ideal for medical use such as self-expandable stents. This is improved by the austenite and martensite structures that form by altering the temperature. Eventually, nitinol is expected to be used for the production of prosthetic limbs because the nanoparticle has been found to attach to stem cells in the body, producing a naturally functioning arm or leg that can be controlled and sensed by the body’s own nervous system. However, the presence of nickel brings concern that the substance, an allergen and possible carcinogen, could be released in the body and could cause more damage. Therefore, the nanoparticles must be treated in a way to reduce the chance of the release of a free radical. A proposed method has been the self-assembled monolayer. Here, phosphonic acid was used to form a film on the nitinol powder, similar to the films used on the metals used in everyday life to prevent oxidation or rust. By varying concentrations of phosphonic acid, the phosphorus content and surface coverage was altered to make the nitinol safer and less reactive in the presence of oxygen, as biomedical tools are required. These modifications were characterized by using scanning electron microscope and energy-dispersive X-ray spectroscopy. Furthermore, powder X-ray diffraction and infrared spectroscopy were used to
characterize the “fingerprint” of the chemicals involved with three dimensional patterns and to identify the presence of the acid.

COLL 154

Modification of zinc oxide nanoparticles with perfluoro phosphonic acids

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Self-Assembled Monolayers (SAMs) were formed on the surface of zinc oxide nanoparticles using different perfluoro phosphonic acids. Infrared spectroscopy (IR) and Scanning Electron Microscope- Energy-Dispersive X-ray Spectroscopy (SEM-EDX) techniques were used to characterize the surface reaction and determine the degree of surface coverage. Solid-state nuclear magnetic resonance (SS-NMR) was used to analyze and determine precisely how the acids bind to the ZnO surface. Furthermore, electrochemical analysis were performed to characterize the redox reaction occurring at the interface. A common problem with modification of nanoparticles is the agglomeration effect that nanoparticles can irreversibly undergo that provide non-specific binding to the molecule and not be as ordered as wanted. Solar panels are highly expensive to fix and repair, with this research, repairs on the solar panels will be fewer and more cost effective. There are also ways this could benefit bio analysis. Diagnostics, chip-based technologies, and screenings can all take advantage of this research which will allow enhanced and more efficient results.

COLL 155

Proton coupled electron transfer through 2-2':6'-2'' terpyridine molecular wire between graphene - gold nanoparticle junction

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Electrostatic repulsion of negatively charged Citrate Capped Gold Nanoparticle (Au\textsubscript{n}\textsuperscript{0}) and Electrochemically reduced graphene (GR) can be mixed by a positively charged interlinker. Here for the first time we have used positively charged Metal Organic Molecular wire (MW) as a linker for the preparation of Au\textsubscript{n}\textsuperscript{0}-MW-GR film on Glassy Carbon electrode\textsuperscript{1}. Highly aniostropic conductive Terpyridine based Metal-Organic molecular wire\textsuperscript{2} is itself well known in solar energy devices and in electrochemical sensing application. The presence of MW linker between Au\textsubscript{n}\textsuperscript{0} and GR increased the electron transfer rate constant and that can be attributed to the Intermolecular proton switching that prescent in the MW. Presence of Metal to Ligand Charge Transfer (MLCT) also take part in the increase of electron transfer rate constant of Au\textsubscript{n}\textsuperscript{0}-MW-GR film. Comparison of Charge transport by depositing above film on glassy carbon and
ITO electrode brings the information about bidirectional electron flow through MW from GR to Au$_n^0$ and vice versa.

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Proton Coupled Electron Transfer between Gold nanoparticle and RGO

**COLL 156**

**Study of thermal diffusivity in metallic and bimetallic Fe and Au nanoparticles**

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The synthesis and characterization of iron nanoparticles (NPs) have been investigated in the last years due to their applications and technological innovations. When suspended in a solution, these NPs can diffuse in response to a temperature gradient, leading to an effect known as thermodiffusion, which can be related with some of the sample characteristics. Several methods of synthesis are reported in the literature, however some of them are more direct than others and present results with different physical-chemical parameters. In this study, metallic and bimetallic Fe and Au nanoparticles were synthesized by the thermodecomposition of coordination compounds. Morphological, structural and magnetic properties of metallic Fe nanoparticles coated with oleic acid, Au and Fe/Au were carried out. The results showed that these NPs have diameter between 5 and 10 nm and Fe NPs display
superparamagnetic behavior at room temperature. There was also the investigation of these systems correlating the synthesis parameters with the characteristics of the produced NPs. These materials were suspended in a liquid carrier and presented nonlinear optical characteristics, such as the nonlinear refractive index (n2) and thermal diffusivity (D), that can be indicated with a technique named Z-Scan. This technique was developed in the early 90s to allow the measurement of some nonlinear parameters with different light intensities going through the sample. Others characterizations were also used as complementary techniques, such as UV-Vis Spectroscopy. Therefore, the combined results gave support to conclude that there were produced nanoparticles with narrow size distribution and these NPs presented nonlinearity mainly guided by the solvent used, presenting themselves as good candidates for the study of thermodiffusion. Acknowledgements: FAPESP, CAPES, CNPq and Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos (INCT-FCx).

COLL 157

Fabrication of liquid-like-surface and evaluation of anti-frosting property

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Icing on surface is a critical issue in various fields. Although there are some anti-icing systems such as electrothermal method at the present time, most of these conventional anti-icing and deicing strategies are often inefficient, energy-consuming, high-cost, or environmentally harmful. Therefore, the previous studies have focused on superhydrophobic surface and slippery liquid infused porous surface (SLIPS) for delaying or preventing ice formation recently. However, it has been reported that these strategies can assist ice formation because of rough structure and lubricant layer. In this study, we focused on liquid-like-surface. The liquid-like-surface which was reported by Hozumi et al. in 2012 can shed off various complex liquid like water and oil. This oleophobicity contributes to an enhancement of the dewetting properties on the surface by increasing the ability of functional groups to move and become liquid-like. We supposed that the liquid-like-surface can overcome problems of superhydrophobic surface and SLIPS, because it has flat surface without rough structure and lubricant layer such as SLIPS and shows oleophobicity. Here, anti-frosting property of liquid-like-surface without rough structures and lubricant layer was studied. Here, we fabricated three kinds of liquid-like-surface modified by Decyltrimethoxysilane (DTMS), Fluoroalkylsilane (FAS13 or FAS17). As the results, liquid-like-surface delayed frost formation comparison with uncoated surface. (Figure 1) In particularly, the liquid-like-surface modified by FAS17 showed performance of delaying frost formation by 45 minutes on subcooling surface. (Figure 2)
Mechanistic study using a quartz crystal microbalance: Effect of spacer length on the antimicrobial activity of the bound peptide, Chrysophsin-1

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Healthcare associated infections (HAIs) cost the US $45 billion dollars annually in direct costs, 60% of which are due to infections associated with medical devices. Currently, these infections are treated with systemic antibiotics, debridement, and implant removal; but the high local antibiotic concentrations needed to kill colonized bacteria are only
achieved over a short time and may be cytotoxic to surrounding cells. The use of antibiotics has the potential to impart antibiotic resistance, which the Center for Disease Control considers a catastrophic threat. We have developed a unique approach to combat implant-associated HAIs with surface-tethered antimicrobial peptides (AMPs) that prevents these infections from occurring in the first place.

Antimicrobial peptides are ideal candidates to combat these infections because they have a low likelihood of causing bacterial resistance due to their mechanisms of action and their broad spectrum activity. One of the major drawbacks of AMPs is their potential cytotoxicity. Tethering the AMPs has been shown to reduce cytotoxicity; however, immobilization of AMPs can reduce their antimicrobial activity. It has been suggested that a longer spacer allows for the flexibility and mobility needed for AMPs to remain active against bacterial pathogens. We have covalently linked the AMP chrysophsin-1 with a cysteine modification to silicon dioxide (SiO₂) using a poly(ethylene glycol) (PEG) spacer molecule to allow flexibility and maintain activity. Three different polyethylene glycol spacers (MW 866, MW 2000, MW 7500) were examined to determine the effect of spacer length on antimicrobial activity. A quartz crystal microbalance with dissipation monitoring (Biolin Scientific, Sweden) was used to monitor the attachment of both the PEG spacer molecules and chrysophsin-1 peptides to SiO₂-coated quartz crystal surfaces in real time. The thickness of the tethered system as well as the density of the peptide was determined using this technique. Thus far, an efficacy of 82+/−11% against gram negative model bacteria, *Escherichia coli* HB101, and 50+/−11% against gram positive bacteria, *Staphylococcus aureus* ATCC43866. Determining the effect of spacer length on antimicrobial activity will help define the mechanism by which the peptide acts, thus allowing for more rational design of antibacterial surfaces as well as improve patient outcomes.

**COLL 159**

**Preparation of lipid bilayer membrane-based nanotubes-enclosed polymer composite film**

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Self-assembling low molecular weight gelators have been attractive as a constructing tool for bottom-up strategy. We have reported that L-glutamide-derived lipids can form nanometric one-dimentional aggregates such as nanotubes, nanohelicies, and nanoribbons in various solvents. Because of effective intermolecular hydrogen bonding, nanometric one-dimentional aggregates can be created in hydrophobic polymer matrix. On the basis of this phenomenon, transparent and optical active polymer-monomer composite films were successfully fabricated in organic system.¹) We also reported that cationic L-glutamide-derived lipids ($g_{12}$-Py⁺) can form quite uniform single-walled bilayer membrane nanotubes in aqueous solution.²) In this paper, we report enclosure of lipid nanotubes in hydrophilic polymer film in aqueous system. $g_{12}$-Py⁺ was dispersed in
water by ultrasonication to produce clear to slightly turbid solutions. After aging at 10 °C for 1 hour, the solution was mixed with polymer aqueous solution. Being dried on the glass slides at room temperature, transparent composite polymer film was obtained. The result of TEM observation indicated that single-walled bilayer membrane nanotubes were constructed in obtained composite polymer film. In this paper, morphological and microenvironmental effect on enclosure of g_{12}-Py^{+} aggregates in polymer matrix will be discussed.

[References]

Figure 1. (a) Structural formula of cationic L-glutamide-delived lipid for creating nanofibrillar aggregates. (b) TEM image of g_{12}-Py^{+} aggregates in polyvinyl alcohol film.
Biomemory regulator device composed of metalloprotein/DNA/nanoparticle

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In this research, biomemory regulator composed of metalloprotein/DNA conjugate and nanoparticle is fabricated. To fabricate the biomemory regulator, a recombinant azurin, blue-copper metalloprotein with cysteine residue, is used as biomemory source because of its redox property. A recombinant azurin is conjugated with single strand DNA (ssDNA) by a bifunctional chemical linker [1, 4-phenylene diisothiocyanate (PDITC)] via chemical ligation method. Also, complementary DNA (cDNA)/ quantum dot (QD) and cDNA/silver nanoparticle (SNP) conjugate is used as input receptor. Conjugation of recombinant azurin and ssDNA is confirmed by sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and agarose gel electrophoresis. A recombinant azurin/ssDNA conjugate is immobilized on Au substrate directly by self-assembly of cysteine residue in azurin. Atomic force microscopy (AFM) is operated to confirm the immobilization of conjugate on Au substrate. With addition of input receptors, cDNA/QD and cDNA/SNP, this fabricated biomemory regulator shows two distinct functions which are ‘biomemory decrement’ and ‘biomemory increment’. Cyclic voltammetry (CV) is used to obtain the redox potential value of biomemory regulator. Then, using obtained redox potential values, biomemory decrement and the biomemory increment functions are performed in agreement with added input receptors. Functions of biomemory regulator, biomemory decrement and the biomemory increment are verified by differential potential voltammetry (DPV) and chronoamperometry (CA). From experimental results, this proposed biomemory regulator composed of recombinant azurin/DNA conjugate with nanoparticles can become a novel tool to develop environment-dependent information processing system applications.

Acknowledgments
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References

Molecular interactions between gold nanoparticles and model cell membranes
Nanoparticles (NPs) have begun to revolutionize the way science and medicine has tackled the most complicated research questions. In the field of biomedicine, NPs have been developed for such applications as diagnosis, targeted drug delivery, cancer therapy. Mechanisms of cellular uptake of NPs still remain unknown, and more specifically, questions about the molecular level response of each leaflet of the cell membrane to NP exposure has not been addressed due to a lack of appropriate surface/interface-sensitive techniques to study such NP-cell membrane interactions in situ in real time. In this study, sum frequency generation (SFG) vibrational spectroscopy was applied to investigate the interactions between lipid bilayers (to mimic model mammalian cell membranes) and gold NPs (Au NPs) of four different sizes at same concentration in terms of NP number, or NP surface area, or mass. It was found that lipid flip-flop was induced by Au NPs of all four sizes. The lipid flip-flop rate increased with increasing NP size based on the same particle number or the same NP surface area whereas it was the same for Au NPs with different sizes with the same mass. Models developed to explain changes in flip flop rates calculated an “effective surface area” defined as the direct contact surface area between Au NPs and the model cell membrane. This study provides direct observation of the initial interactions of between Au NPs and the model mammalian cell membrane at the molecular level.

**COLL 162**

**Design of well-defined thermoresponsive glycopolymer micelles from enzymatic synthesis-RAFT polymerization for biological recognition**

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Great emphasis has been placed on the well-defined glycopolymers for the exploration and mimic of cell surface-saccharide interactions in recent years, which are critical components of diverse biological processes. This study aims at developing a facile and effective strategy for the designing of well-defined thermoresponsive glycopolymer micelles based on enzymatic synthesis and RAFT polymerization. The shape, size, appropriate sugar spacing and density of thermoresponsive glycopolymer micelles are expected to be well controlled by changing temperature and the chemical structure of glycopolymers, including the refined structure of the glycosyl monomer (connection arm structure and various kinds of saccharides et. al), in order to investigate the effect of the structure on the behavior of self-assembling in aqueous phase. Based on these researches, the influence of the chemical structure and composition of micelles on the targeted special recognition interaction between glycosylated surface and protein multivalence binding force will be evaluated. The relationship between structures and targeting effect of synthesized well-defined thermoresponsive glycopolymer micelles on hepatic cells are studied in details by in vitro cell biological assays. This project could be applied to simulate the biological behavior of mass transfer between inner and outsider...
of cells, with potential application in building a "conversation" bridge between artificial intelligent materials and the real cells.

COLL 163

Making colors from black and white

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This paper addresses recent developments in structurally colored materials composed of submicrometer-sized fine particles, where the structural color is not angle-dependent. Recently, studies on colloidal crystals of submicrometer-sized fine particles for structurally colored materials applications have drawn great attention. Materials researchers have become aware that many living things exhibit bright structural colors that arise from amorphous arrays of particles, pores, and fibers and are now engaged in research related to this phenomenon. In particular, colloidal amorphous arrays composed of submicrometer-sized fine particles, which can display vivid structural color without angle dependence, have become a popular topic of study within recent years. In this paper, I review the possibility of using colloidal amorphous arrays as stimuli-responsive colored materials based on the properties of colloidal amorphous arrays that have been elucidated in recent experimental investigations.

COLL 164

Gene delivery by polyethylenimine-functionalized graphene oxide suppresses breast cancer cell migration

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The carbon-based nanomaterial graphene can be chemically modified to associate with various molecules such as chemicals and biomolecules, and developed as novel carriers for drug and gene delivery. In this study, a nonviral gene transfection reagent was produced by functionalizing graphene oxide (GO) with a polycationic polymer, polyethylenimine (PEI), to increase the biocompatibility of GO and to interact electrostatically with the negatively charged phosphate groups in nucleic acids. PEI-functionalized GO (PEI-GO) was a homogeneous aqueous solution that remained in suspension during storage at 4°C for at least 2 months. The weight percentage of grafted PEI and particle size of PEI-GO were characterized by thermogravimetric analysis (TGA) and dynamic light scattering, while binding affinity of PEI-GO toward small interfering RNA (siRNA) was assessed by electrophoretic mobility shift assay (EMSA). With the GO-based gene carrier, we transfected the invasive breast cancer cell line, MDA-MB-231 cells with siRNAs against C-X-C chemokine receptor type 4
CXCR4, a biomarker for cancer metastasis. Suppression of the mRNA and protein expression of CXCR4 by siRNA was confirmed by real-time PCR and western blot analysis. Transfection efficiency of PEI-GO was comparable to that of a common transfection reagent, Lipofectamine 2000. Through migration and invasion assays, we demonstrated that the metastatic potential of MDA-MB-231 cells was suppressed by siRNAs against CXCR4 (siCXCR4) delivered by PEI-GO. Our results suggest that PEI-GO is a potentially efficient, nonviral transfection reagent that may contribute to cancer therapy.

**COLL 165**

**QCM-D based mechanistic study of Alzheimer’s disease: Membrane-amyloid peptide interactions**

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Structural transition of amyloid β peptide (Aβ) into the β-sheet state followed by amyloid fibril formation is the cause of a significant step in the pathogenesis of Alzheimer’s disease (AD). Numerous studies have demonstrated that lipid membrane surfaces promote the conversion of amyloidoigenic proteins into misfolded toxic aggregates, and eventually these aggregates destabilize the structural integrity of the cell membrane. The main objective of this research is quantitative study of amyloid peptide-membrane interactions. Moreover both the aggregation process as well as the membrane destabilization process is studied. An important membrane model is a supported lipid bilayer (SLB). Such a model can be conveniently probed using quartz crystal microbalance with dissipation (QCM-D) technique. Here a QCM-D technique is employed to understand the fibril formation process and the consequent structural change of the membrane. In this QCM-D measurement, a supported lipid bilayer (SLB) is deposited on the surface of an SiO₂-coated quartz crystal and Aβ aggregation intermediates are introduced in the bulk solution above the crystal to initiate interaction between the SLB and the protein. This research helps us to study the formation of amyloids and their related toxicity to understand the onset and progression of the neurodegenerative diseases. The cause of most neurodegenerative diseases such as Alzheimer’s disease has been poorly understood. Understanding the cause of this disease would be the first step in developing therapeutics.

**COLL 166**

**2D nanoparticle cluster formation in supercritical fluid CO₂**

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Abstract
Supercritical fluid carbon dioxide is capable of depositing nanoparticles in small structures of silicon wafer because of its gas-like penetration and liquid-like density abilities and near zero surface tension. In small shallow wells on silicon surface, formation of two-dimensional monolayer nanoparticle cluster arrays can be achieved using the supercritical fluid deposition method. Nanoparticles fill nano-structured holes first, and then, if there are more nanoparticles available, they will continue to cover the areas nearby, unless defect areas are available. SEM pictures of two-dimensional gold nanoparticle arrays formed on silicon wafer surface with three to a dozen or more nanoparticles are presented to illustrate the patterns of nanoparticle cluster array formation in supercritical fluid carbon dioxide.

COLL 167

Effect of incorporation of lysolipid on the stability of dipalmitoyl phosphatidyl choline bilayer membrane: Molecular dynamics simulation approach

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Drug delivery and its release depend greatly on the ability to control the permeability of the vesicle encapsulating the drug. Liposomes, which are spherical nanoparticles composed of one or more phospholipid bilayers, have emerged as a promising delivery system for potent chemotherapeutics. It is well known that the permeability of drug through lipid bilayers exhibits a maximum as the lipid bilayer undergoes the transition from gel to liquid-crystalline phase, which has been studied intensively in order to control the permeability. One of the ways for the controlled drug release is an addition of the lysolipid, which affects the transition properties such as temperature.

In this study, we run fully atomistic molecular dynamics (MD) simulations with flat liposome model comprised of both dipalmitoyl phosphatidyl choline (DPPC) and 0-30% lysolipids of monopalmitoyl phosphatidyl choline (MPPC). The stability of the lipid bilayer is investigated by monitoring energy, density profile, area per lipid molecule and the lateral diffusion coefficient as the temperature is changed. Through this study, we attempt to clarify the most probable distribution of MPPC in the mixed membrane.

COLL 168

Magneto-fluorescent core-shell supernanoparticles
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The design and fabrication of materials that simultaneously contain more than one type of functional components, so-called multifunctional materials, is an active research area with the potential to impact a wide range of technological applications. In particular, co-assembling two types of nanocrystals with distinct properties into larger colloidal particles, especially at the mesoscopic scale, offers the possibility of producing new classes of nanoparticles (i.e., supernanoparticles, SPs) with a set of combined properties, all the while maintaining the colloidal nature of their building blocks. Here, we report a simple and effective method for assembling CdSe-CdS QDs with Fe$_3$O$_4$ MNPs into colloidal SPs with a “core-shell” (CS) superstructure. Additional thermal annealing drives the crystallization of the “core” MNPs into a highly ordered supercrystal with an ideal fcc superlattice. The CS-SPs can be easily coated with a thin silica layer, providing surface functionality and colloidal stability as well as biocompatibility. Importantly, these silica-coated CS-SPs for the first time simultaneously satisfy all the design criteria needed for various applications: uniform and tunable sizes, high magnetic content loading, maximized fluorophore loading on the surface, substantial colloidal stability, and versatile surface functionality. These features allow the utilization of these magneto-fluorescent SPs for \textit{in vitro} intracellular manipulation and \textit{in vivo} MR/MP dual-modal imaging.

COLL 169

DNA-polypeptide polyplexes

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Polyplexes, also known as polyelectrolyte complexes are polymer-rich phases that form upon mixing oppositely charged polyelectrolytes in solution. Known types of polyplex include liquid-like phases called coacervates and solid precipitates. Core-shell micelles can also form if at least one of the polymers is a block copolymer with a hydrophilic tail; these are often called polyplex micelles. While it has been shown that both electrostatic and entropic forces drive polyplex formation, the relationships between the properties of the complexes and those of the component polymers are not fully understood. In this work, we study polyplex formation between DNA oligonucleotides and positively charged oligopeptides such as poly-L-lysine. By controlling the length and sequence of both polymers, as well as the hybridization state of the DNA, we are able to precisely probe the conditions at which the DNA-polypeptide complexes phase separate, the types of complex that are produced, and the properties of the complexes. We characterize the complexes with multiple methods, including spectrophotometry and optical microscopy, and measure their properties as functions of stoichiometry and ionic strength. Interestingly, we find that the complexes are very sensitive to the hybridization state of the DNA (single vs. double-stranded), a particularly important parameter.
because nucleic acid–peptide micelles are an attractive vehicle for delivering therapeutic molecules such as siRNAs to cells.

**COLL 170**

**Upconversion of trapped charge carriers in coupled lead sulfide quantum dot solids**

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Lead sulfide (PbS) colloidal quantum dots (QDs) are a promising material for infrared optoelectronic devices. Understanding charge transport in these complex inorganic-organic solids is crucial to designing more efficient devices. Currently, QD photovoltaic device efficiency is believed to be limited by charge carrier recombination at surface defect trap states which are energetically located within the band gap. However, this work observes direct excitation of trap states followed by upconversion to the band edge state in coupled thin films of highly monodisperse PbS QDs using transient absorption spectroscopy. Varying the excitation wavelength elucidates the trap state spectral shape and its overlap with the band edge state. Using a series of thiol ligands of varying length, it is found that while absorption occurs for QD solids with any ligand length, upconversion occurs only for strongly coupled QD solids. The effects of temperature and QD size on the upconversion process are also discussed.

**COLL 171**

**Mechanisms of metal deposition on colloidal gold nanoparticle substrates**

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Multimetallic nanoparticle architectures have been shown to synergistically combine properties of their constituent materials. One attractive class of these materials is the combination of plasmonically active nanoparticles as substrates for other catalytic or magnetic materials. Architectures of these secondary components are often either templated by the underlying structure (e.g. core-shell or “framed” nanoparticle colloids) or by an external template (e.g. porous anodized aluminum oxide). Here, we leverage nanoparticle surface chemistry to create arrays of discrete 2D nanoparticles directly on the surface of a colloidal plasmonic nanoparticle substrate. The reaction is monitored by electron microscopy techniques, as well as X-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy, and X-ray crystallography. Our results elucidate critical parameters that affect the growth, oxidation, and metal intermixing processes observed in multimetallic systems for the construction of nanoscale photocatalysts.

**COLL 172**
Light scattering from concentrated eye lens beta crystallin solutions

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Beta crystallin is one of the eye lens proteins involved in cataract, a leading cause of blindness. The clouding of the eye in cataract depends on the strength of attractions and repulsions between its constituent proteins. This work studies forces between beta crystallins, to help quantitatively understand how those forces might be related to eye lens transparency. Bovine beta crystallin fractions were isolated using size-exclusion chromatography of 1-2 week old calf lens cortical homogenates, and studied using static and quasielastic light scattering at 633 nm wavelength, up to concentrations of 250 milligrams/milliter (mg/ml). These measurements yield excess Rayleigh ratios, or absolute cross sections for light scattering, and corresponding collective diffusion coefficients. For higher beta crystallin molecular weight fractions averaging 7x10\textsuperscript{4} grams/mole, as measured by light scattering at low concentration, high concentration Rayleigh ratios plateau in the vicinity of 200 to 250 mg/ml, at close to 1.5 x 10\textsuperscript{-3} inverse centimeters. Collective diffusion coefficients are approximately constant at 5.5 x 10\textsuperscript{-7} cm\textsuperscript{2}/sec over an extended concentration range, before decreasing at the highest concentrations. We find that the Carnahan-Starling equation of state provides a useful approximation to the observed Rayleigh ratios within this concentration range. Thus the observed dependence of the Rayleigh ratios on concentration is approximately consistent with the influence of repulsive, hard-core interactions between beta crystallins.

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pH Sensitive delivery of Pt\textsuperscript{2+} based therapeutics in lipid-coated PLGA nanoparticles

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Our goal is to develop new Pt\textsuperscript{2+}-containing complexes incorporated into a nanoparticle (NP) carrier at high payloads. We validated the biologic effectiveness of the NP in an ovarian cancer model. We explored two classes of Pt\textsuperscript{2+}-complexes: a carboxylate and imidazole. The pH sensitivity of the platform provides slow and fast aquation rates of the complexes at physiological and tumoral pH, respectively. The Pt\textsuperscript{2+}-complexes are synthesized from malonic acid and biimidazole derivatives and a Pt\textsuperscript{2+} precursor and
then chemically attached to modified poly(lactic-co-glycolic) (PLGA) polymer using click chemistry. The lipid-coated PLGA NPs are formed via the nanoprecipitation method. NPs have a size of 187 nm with low polydispersity (0.159). Encapsulation efficiency is 4.5% wt/wt Pt/PLGA. Preliminary biologic testing in the isogenic ovarian cancer cell lines A2780 and A2780-CP70 (cisplatinum resistant) demonstrates 50% increased cell death at NP concentrations five times lower "than commercially used free cisplatin."

COLL 174

Sum frequency generation spectroscopy of nanomaterial interfaces: Applications in photovoltaics and sensing

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A concentration dependent surfactant solubilization of size selective single walled carbon nanotube has been investigated using silica substrates. C-H and C-D stretching in the IR region has been monitored by VSFG spectroscopy. Sodium dodecyl sulfate (SDS) and deuterated sodium dodecyl sulfate (SDS-d₂₅) were used for solubilization of single walled carbon nanotube (SWCNT) bearing chirality (7,6). Different concentrations of surfactants were used to exfoliate and solubilize SWCNT(7,6) and were spin coated on silica substrate. The orientation of the surfactant on the nanotube surface was investigated by monitoring the C-D symmetric and asymmetric stretch modes. Preliminary analysis and fittings of the surfactant-carbon nanotube interface provide important insights on the concentration dependent orientation of the surfactant over the nanotube walls. This is very significant in understanding the mechanism behind exfoliation and solubilization of single walled carbon nanotubes and their eventual application in size sorted pure nanotube separation, photovoltaics and energy harvesting. In a similar approach buckminsterfullerene (C60) was spin casted over gold and silica substrate for investigating the symmetric pentagonal pinch mode with variable visible excitation wavelengths at the air-solid interface. The resultant electronic transition features coupled to the pentagonal pinch modes were monitored with respect to surface interaction of fullerene molecules.

COLL 175

Smart drug delivery system using magnetic core-shell gold nanoparticles

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Owing to the high cytotoxicity of chemotherapeutic drugs, extensive efforts have recently been made to develop new regimes for tumor tissue annihilation that would prevent damage to healthy cells. One such prospective technology is based on targeted nanoparticle drug delivery enabling accumulation of the injected drug-loaded nanocarriers in tumors, thus limiting the drug toxicity to other tissues. In this work, we have investigated a novel smart drug delivery system for anticancer drugs, including doxorubicin (DOX), mitoxantrone (MXT), and 5-fluorouracil (5-FU), based on functionalized core-shell magnetic Fe$_2$Ni@Au nanoparticle carriers. The drugs were immobilized on magnetic nanoparticles (MNPs) through their surface functionalization with active thiol self-assembled monolayers (SAM). The drug release from MNPs was monitored using surface-enhanced resonance Raman scattering spectroscopy (SERRS) utilizing Raman probe molecules embedded in the NP shell. The electrochemical detection methods were also employed. The results have shown that most of the drug release was completed within first 4 hours of the release time. The rate of release was higher at pH less or equal to 5.3, corresponding to the cancer cell pH. In further studies, the reduced folate and anticancer drugs were immobilized on MNP carriers. In this way, the carriers can recognize cancer cells due to the overexpressed folate receptors in tumors. They can also be accumulated in the target cancer tissue by focusing magnetic fields. The proposed method should be able to decrease the drug dispersion in healthy tissues with blood stream and reduce dramatically the side effects of highly toxic anticancer drugs.

COLL 176

Preparation of modified poly(ethylene-co-acrylic acid) (PEAA) usary ammonium with aliphatic chains as antibacterial polymer

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Poly(ethylene-co-acrylic acid) (PEAA) was modified from dimethylethanolamine (DMAE) and 1-chlorododecane were prepared as antibacterial polymer. A two-step reaction was conducted. First, PEAA was swelled and dissolved in solvent. After that DMAE was grafted onto PEAA with esterification using catalyst such as sulfuric acid. Second, 1-chlorododecane was added and combined with amine by S$_{N}$2 reaction. There were changed reaction time, temperature, amount of reactant and catalyst for optimal point of the modified PEAA. The final product had quaternary ammonium with positive charge and was made to film as food package. Also, it was tested for antibacterial. All these process were examined to infrared spectroscopy (IR), nuclear magnetic resonance (NMR).

COLL 177

Interpenetrating network polymer gel for improving oil recovery
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Excessive water production is one of the major challenges in mature oilfield recovery. To reduce water cut, thereby enhance oil recovery, an effective remediation is injecting crosslinked hydrogel to block the existed high permeability zone. In this procedure, an intensively used material is polyacrylamide (PAM) based hydrogel in common reservoir. However, in formidable formation conditions, such as high temperature and high salinity, PAM hydrogel are not applicable. Therefore, a polyvinyl alcohol (PVA) and PAM interpenetrating polymer network (IPN) gels with two different crosslinking structures were designed to address the natural throwback of pure PAM gel.

In this work, we investigated the swelling capacity of PVA/PAM IPN gel under different environments; measured the viscoelasticity of the gel; and examined the effects generated by pH and salinity. Scanning electrical microscope (SEM) was implemented to observe the microstructure and thermal stability tests were conducted through thermal gravimetric analysis (TGA). To furtherly approach to real formation environment, thermal stability of IPN gel in aqueous condition which combined high temperature and high salinity has been evaluated. The results indicated that, due to the presence of second network, gel properties involving acid resistance, salinity resistance and mechanical strength have been significantly improved. PVA/PAM IPN gel was also turned out to have potential to maintain thermal stable in 80°C and 10,000 ppm NaCl brine for at least 80 days.

Keyword: enhance oil recovery; hydrogel; interpenetrating network polymer;

COLL 178

Tunable intermolecular interaction in N-methylfulleropyrrolidine (8-NMFP) mediated with assembly of gold nanoparticles

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The ability to make size- and shape-controllable architectures using macromolecule as building block is important for the exploration of nanoparticle-structured properties. Fullerene-C\textsubscript{60} and its derivatives exhibit a wide variety of distinct properties, like superconductivity, magnetic, electrochemical and optical. Fullerene-C\textsubscript{60} reacts with nucleophiles enthusiastically due to its electron deficient nature and is a reactive double bond component in cycloaddition reactions [1-3]. The numbers of pyrrolidine moieties on fullerene-C\textsubscript{60} surface can be controlled synthetically and chemically. The present work emphasizes on functionalization of fullerene-C\textsubscript{60} surface under very controllable reaction conditions. Afterwards, synthesis of their nanocomposites with 3-mercaptopropanioic acid ligand capped gold nanoparticles provided opportunities for studying the fine tunable interparticle interaction and process of controllable macromolecular assembly and disassembly. The non-covalent (electrostatic) interaction
between fullerene-C₆₀ derivatives with 3-mercapto propanoic acid capped gold nanoparticles created 3D nanostructures with distinct optical and spectroscopic tunabilities corresponding to the surface plasmon band and pH conditions. The interaction between 8-NMFP with 3-mercapto propionic acid capped gold nanocomposites was computed using DFT method.

References

Novel photothermal-based release mechanism for controlled release on Au nanoparticles through light

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Noble metal nanoparticles, especially gold nanospheres (AuNPs) ones, possess strong visible light absorption due to their localized surface plasmon resonance (LSPR) characteristics [1]. They have strong absorption in the visible region while maintaining a compact size. On exposure to a laser beam with a wavelength that matches the absorption peak of the Au nanoparticle, the light will be absorbed and converted into heat through the photothermal effect [3, 4]. Here we developed a novel drug release method based on the photothermal effect of gold nanoparticles. We demonstrated the precisely controlled delivery of a molecule from AuNPs via cleaving the thermolabile chemical bonds by controlling the power density and irradiation time of the light source.

Gold nanospheres were synthesized by using chemical reduction method [2]. The thermolabile molecules used in this study contain thermolabile covalent bond and a link group for gold conjugation. We used an organic dye for the release study due to easy detection of the released cargo by using UV-Vis spectrophotometer.

The release of the dye from thermolabile molecules on the AuNPs demonstrated using different power density of a laser at constant duration or constant power density at different duration by cleaving thermolabile linkage with generated heat. When the laser is turned off, heating will immediately cease. We can control the release dosage by manipulating the power density and/or irradiation time of laser. After successful dye release trials, a thermolabile molecule containing a cancer therapeutic agent was synthesized in a similar way as dye containing molecule and further studies are under investigation.

ACKNOWLEDGEMENTS
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References

COLL 180

Omniphilic superparamagnetic iron oxide core-shell nanoparticles

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Using nanoparticles, especially for biomedical applications, requires close control over nanoparticle–cell interactions which are mainly dictated by shape, size, surface ligand and charge of the nanoparticles.\(^1\) We have synthesized highly monodisperse superparamagnetic iron oxide nanoparticles coated with a shell of Y-shaped amphiphilic
ligands grafted irreversibly and at high density using nitroDOPA as anchor.\textsuperscript{2} This ligand consists of two rigid arms attached to a single anchor terminated by one hydrophobic and one hydrophilic group terminated respectively. Thus, the exact ratio of hydrophilic to hydrophobic surface area on the particles can be controlled on the sub-nanometer scale by arm length and hydrophilicity of the end-groups. It has been suggested that nanoparticles with randomly or locally ordered mixed ligand shells display solubility in both nonpolar and polar liquids\textsuperscript{3} and thereby prevent adsorption of proteins and can enter cells in a non-disruptive way.\textsuperscript{4} Our approach, using Y-shaped and irreversibly linked rigid ligands comprises a platform where these effects can be experimentally investigated without rearrangement of the shell or loss of ligand due to changes in the environment. We present the chemical and colloidal characterization of these novel nanoparticles.


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\includegraphics[width=0.5\textwidth]{ligand.png}
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\textbf{COLL 181}

\textit{Understanding the effect of TMA\textsuperscript{+} on the condensation behavior of [H\textsubscript{2}Ta\textsubscript{6}O\textsubscript{19}]\textsuperscript{6-}}
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We have found that high density tantalum oxide (Ta₂O₅) films can be deposited from aqueous solutions of [(CH₃)₄N⁺]₆[H₂Ta₆O₁₀], despite the very significant volume change associated with converting the precursor to the final Ta₂O₅ product. Film qualities have been assessed by X-ray reflectivity and spectroscopic ellipsometry. The transformation of the precursor to film has been followed by temperature programmed desorption measurements. Together, these techniques illuminate the reaction pathway that leads to dense, ultra-smooth Ta₂O₅ films of interest as antireflective coatings and corrosion barriers.

COLL 182

Size-dependent cellular uptake of sub-10 nm zwitterionic gold nanoparticles

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Gold nanoparticles (AuNP) have emerged as a promising platform for a myriad of biomedical applications including drug delivery and disease diagnosis. The physicochemical properties of AuNP essentially dictate the intracellular uptake and therapeutic efficacy of nanoparticles. Considerable attention has been drawn on how the size of NP affects its cellular uptake. However, a majority of previous studies were concluded using either positively or negatively charged NP. These charged NP inevitably have strong interactions with serum proteins, which result in a significant change of physical properties of NPs, thus eventually complicating the understanding and prediction of the correlation between NP size and their interaction with cells. We designed a series of zwitterionic NPs with varied core size, which allowed a systematic assessment of the cellular uptake efficiency directly caused by NP size. We will discuss the results of these uptake experiments, as well as the implications of these studies for nanobiology.

COLL 183

Assembling discrete nanoparticle clusters via weakly interacting DNA linkages

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This presentation focuses on preparing clusters of gold nanoparticles with defined stoichiometry and symmetry. In our work, gold nanoparticles with sizes between 5 - 50 nm are assembled via DNA mediated interactions. The self-assembly kinetics are altered by manipulating interparticle energetics by changing DNA coverage, length, rigidity, and sequence, as well as and nanoparticle size. The self-assembled clusters are collecting after appropriate reaction times, and purified via ultracentrifugation. The conditions for such assembly and purification will be discussed. The assembled clusters were characterized via dynamic light scattering (DLS), UV-visible spectrophotometry (UV-vis) and fluorescence spectroscopy. The morphology of the clusters were characterized by transmission electron microscopy (TEM) and in-situ cryo-TEM. We thank the AFOSR for support of this project (FA9550-10-1-0033) and the NSF for support via an IGERT training grant (DGE-1068780).

COLL 184

Understanding the assembly and aligning of semiconductive quantum rods on DNA origami

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In this presentation we will describe the DNA-mediated self-assembly of CdSe/CdS quantum rods (QRs) onto DNA origami. We are interested in using origami to organize rods with controlled spacing and orientations, the result of which will determine the optical response. Two QR types with unique optical emission and high polarization were synthesized, and then functionalized with oligonucleotides (ssDNA) using a novel protection-deprotection approach, which harnessed ssDNA’s tailorable rigidity and denaturation temperature to increase DNA coverage by reducing non-specific coordination and wrapping. The QR assembly was programmable, and occurred at two different assembly zones that had capture strands in parallel alignments. The QR-origami conjugates could be purified via sucrose gradient ultracentrifugation. Assembly yields, QR stoichiometry and orientation, as well as energy transfer implications were studied in light of QR distances, origami flexibility, and conditions. Recent studies using hexagonal- and square-lattice origami will also be discussed. We thank the AFOSR for support of this work (FA9550-10-1-0033).

COLL 185

Designing stable foams in the presence of alkanes and brine for oil field operations

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Decrease of foam stability due to crude oil present in subsurface is considered one of the challenges in applying foam technology in oil reservoirs. This endeavour explored the effects of the presence of different alkanes and elevated brine levels on surfactant-based foam stability. Use of co-solvent or nonionic co-surfactant(s) are also investigated to improve the performance of foams. The stability of foam generated was determined by purging the selected gas through a certain amount of surfactant solution in a glass column. The resulting foam height was monitored as a function of time. Two anionic C15-18 Internal olefin sulfonate (IOS) and sodium dodecyl benzene sulfonate (SDBS) were selected as the foam boosters in this study. For the impact of different alkanes, n-hexane, n-dodecane and n-hexadecane were tested and the results showed that addition of alkanes tends to destabilize the integrity of foam. The foams were more stable in the presence of n-hexadecane as compared to alkanes with shorter carbon chain. At elevated brine concentrations, foams collapsed rapidly when IOS was used when brine concentrations greater than 5 wt.%. Under similar condition, the SDBS solution became unstable and precipitated and could not generate foam in brine. Addition of n-dodecanol drastically increases the foam stability for IOS, even in contact with n-hexadecane. At elevated brine, two types of nonionic surfactant were used to enhance foam stability. Introducing nonionic surfactant in SDBS and brine mixture effectively restrained adverse precipitation behavior and also helped foam generation. Increase of nonionic surfactant concentration tends to have positive impact on foam stability for both surfactants tested. The efficacy of different nonionic surfactants may also be quite different for these two foam boosters (IOS and SDBS).

Vitamin E- conjugated lipidic mixed micellar system as nanocarrier for the delivery of curcumin in cancer

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Micelles are self-assembled colloidal particles with the size in nanometer range, in which many small hydrophobic molecules self-assemble spontaneously. The size of micelles permits their extravasation and accumulation in a variety of pathological sites, where the permeability of the vascular endothelium is increased, such as infarct zones and tumors.

In the present study, we have developed a vitamin E - conjugated lipid-based co-polymer by conjugating two hydrophobic moieties, phosphatidylethanolamine (PE) and α-tocopherol with poly(ethylene glycol) via an amino acid linkage as shown in Figure 1. The synthesized polymers were characterized by IR and H1 NMR spectroscopy. The micelles size and surface charge size were measured by Zetasizer. The mean hydrodynamic diameter of Vit-E/PEG conjugated polymeric micelles (VPM) were 140 nm when compared to PEG-PE micelles (PPM) (21 nm.). Critical micelles concentrations (CMC) for the both the samples was found to be 25 µM. Therefore curcumin was loaded as a model hydrophobic drug and evaluated for drug loading,
stability, in vitro release. Cellular uptake study indicated that the VPM were taken up by cancer cells with similar efficacy compared to PPM and exhibited improved drug loading. The therapeutic efficacy of the newly developed curcumin loaded mixed micellar system will be assessed in vitro in various cancer cell lines and in vivo by using cancer cell xenograft mouse model.

Figure 1. Schematic of the Vitamin E based polymer

COLL 187

Modification of graphene oxide flakes to produce room temperature nanomagnetism

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Several extraordinary properties of Graphene (G) have recently been investigated such as their conductivity, mechanical, thermal, and optical properties. Even though these unique properties of G have been explored, there remain many questions to be answered, particularly with regards to the magnetic properties. Moreover, only a few limited experimental studies exist that explore their magnetic properties and these experiments dealt with G on a substrate rather than as "flakes", or with Graphene Oxide (GO) flakes modified by thermal annealing or adatoms instead of direct chemical functionalization. Therefore, we chose to examine the properties of the flakes of GO before and after their "chemical modification" in order to systemically investigate the impact of such changes on their magnetic properties. By adding these means of modifying graphene's magnetic properties to the already known methods for GO, we seek to open a new field for graphene-based materials for device applications such as spintronic, magnetoresistance, and magnetic memory devices. The GO samples were analyzed by Vibrating Sample Magnetometer (VSM), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Solid Nuclear Magnetic Resonance (Solid NMR).
Antibacterial efficacy of carbohydrate-conjugated nanomaterials

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We are developing glyconanomaterials as novel antimicrobial agents. In this study, we investigate the impact of carbohydrates on the enhancement of antibacterial activity of nanomaterials. Gold, silver and fluorescent silica nanoparticles were synthesized, and functionalized with different mono-, di- and oligosaccharides. These glyconanomaterials were characterized by TEM, SEM, DLS, TGA and IR spectroscopy. Antibacterial efficacy of the nanoparticles against a series of drug resistant bacteria were determined using antimicrobial assays, confocal microscopy and TEM.

COLL 189

Preparation of double emulsions using hybrid polymer/silica particles: New Pickering emulsifiers with adjustable surface wettability

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A facile route for the preparation of water-in-oil-in-water (w/o/w) double emulsions is described for three model oils using fumed silica particles coated with poly(ethylene imine) (PEI). The surface wettability of such hybrid PEI/silica particles can be systematically adjusted by (i) increasing the adsorbed amount of PEI and (ii) addition of 1-undecanal to the oil phase prior to homogenization. In the absence of this long-chain aldehyde, PEI/silica hybrid particles (PEI/silica mass ratio = 0.50) produce o/w Pickering emulsions in all cases. In the presence of 1-undecanal, this reagent reacts with the primary and secondary amine groups on the PEI chains via Schiff base chemistry, which can render the PEI/silica hybrid particles sufficiently hydrophobic to stabilize w/o Pickering emulsions at 20°C. Gas chromatography, 1H NMR and x-ray photoelectron spectroscopy provide compelling experimental evidence for this in situ surface reaction, while a significant increase in the water contact angle indicates markedly greater hydrophobic character for the PEI/silica hybrid particles. However, when PEI/silica hybrid particles are prepared using a relatively low adsorbed amount of PEI (PEI/silica mass ratio = 0.075) only o/w Pickering emulsions are obtained, since the extent of surface modification achieved using this Schiff base chemistry is insufficient. Fluorescence microscopy and laser diffraction studies confirm that highly stable w/o/w
double emulsions can be achieved for all three model oils, and dye release from the internal aqueous cores into the aqueous continuous phase was monitored by visible absorption spectroscopy.

COLL 190

Blockcopolymer based cross linkable surfactant for preparation of polymeric nanoparticles by miniemulsion process

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Polymeric nanoparticles (PNPs) have been attracting great interests in the field of adhesive, magnetics, and biotechnology, especially in delivery system. Among the various preparation methods, miniemulsion process is one of the most popular methods because it can provide multi-gram scale of stable and monodispersed PNPs by relatively easy process. Also, this method give quite flexible possibilities for the cargo material with high loading capacity. However, those emulsions can be degraded with time by Ostwald ripening or coalescence process. To overcome this instability, various kinds of surfactants are studied. Among the surfactants, the polymeric surfactant has advantages to stabilize emulsion even at highly diluted system and more defined surface chemistry. In this study, HPMA/LMA based block copolymer was used as a polymeric surfactant. Also, reversible photo-cross linker moiety is introduced for further increased stability of
emulsion. The increased stability after cross linking was monitored by size and shape change after addition of known stable surfactant and core-dissolving solvent, using DLS, UV/VIS spectroscopy and SEM images.

Schematic draw for the miniemulsion process with photo cross linking.

**COLL 191**

**Silica supported zirconaziridine for hydroaminoalkylation of olefin: Evidences for the mechanism**

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Using the concept of surface organometallic chemistry, we have figured out the mechanism of intermolecular hydroaminoalkylation reaction; Starting from the well-defined 3-membered metallacycle \([≡\text{Si-O-Zr}(\text{HNMe}_2)(\eta^2\text{NMeCH}_2)(\text{NMe}_2)]\), we isolated the 5-membered metallacycle intermediate \([≡\text{Si-O-}\)
Zr(HNMe2)(η^2NMeCH2(Me)CH2)(NMe2)], which was fully characterized by elemental analysis, FTIR, $^1$H-$^{13}$C HETCOR, DARR SS NMR and DQ TQ SS NMR. It unambiguously confirms the selectively 1,2-insertion of the alkene in the Zr-C bond of the 3-membered metallacycle. The regeneration of the catalyst was conducted by dimethylamine protonolysis and affords pure amine.

**COLL 192**

**Low water activity materials for moisture harvesting**

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A new material was made by confinement of low water activity materials (LWA) within superhydrophilic matrix that can allow sustained, removal of moisture and harvesting of clean water from air. The low water activity creates a chemical potential gradient for water vapor near the surface of the materials, while the superhydrophilic matrix promotes micro-condensation and wicks excess water before penetrating into the LWA material. Thus, sustained water harvesting can be attained at roughly 0.5kg/kg-1day at 60% relative humidity at 25oC, without the need for refrigeration cooling or heat regeneration. This provide a potential solution to energy demand in space cooling and conditioning.

**COLL 193**

**Shape control of mesoporous silica nanomaterials and their antibacterial activities**

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Mesoporous silica nanomaterials (MSNs) have attracted a great attention for their wide range of potential applications, especially in biomedical fields. However, little attention was focused on the interaction of MSNs with bacteria. More and more recent evidences, both theoretical and experimental, have showed that the particle shape plays a critical role in mediating the biological effects of MSNs.$^{1-3}$ Therefore, it is of high interest to extend the shape scopes of MSNs and investigate the impact of shape on their antibacterial activities.

By simply tuning the mole ratio of dual cationic surfactant templates, cetyltrimethylammonium bromide (CTAB) and tetrabutylammonium iodine (TBAI), we
successfully synthesized a series of MSNs with various shapes, including film, platelet, sphere, and rod. These MSNs were tested against mycobacteria (*M. smegmatis* strain mc^2^ 651) to study the role of particle shape on their antibacterial activities. The results showed that film-like MSNs possessed relatively higher antibacterial performance than other shapes due to the specific edge-contact interactions.

**References:**

**COLL 194**

**Study of the relationship between cationic degree and the performance of nanoparticle dispersion**

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Positive and negative charges on nanoparticle surface can change the stability of nanoparticle dispersion. In this research, nanoparticles with different cationic degree were synthesized through inverse microemulsion polymerization. [2-(acryloyloxy)ethyl]trimethyl-ammonium chloride (AETAC) and acrylamide were used as monomers and N,N’-methylene bisacrylamide worked as crosslinker. After polymerization, nanoparticles were washed by acetone and filtrate by membrane before test. Zeta potential of the dispersion was measured by dynamic lighting scattering. The contribution of the cationic monomer concentration to surface charge was evaluated. Furthermore, the effect of salt concentration to Zeta potential and the particles size distribution were measured to determine the stability of the system. Viscosities of dispersions with different cationic degree nanoparticles were measured to determine the effect of surface charge.

**COLL 195**

**Poly(ethylene glycol)-bolaamphiphiles for highly stabilized liposomes**

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Sterically stabilized liposomes have received widespread attention as drug delivery vehicles. They are traditionally prepared with poly(ethylene glycol)-(PEG-) lipids, where the lipid portion is embedded within the lipid bilayers as an anchor and the PEG segment provides a hydrophilic spatial barrier that prevents liposome aggregation and fast clearance *in vivo*. However, these protective effects are compromised upon
systemic administration due to low retention of PEG-lipids within membrane upon dilution. Bolaamphiphiles (bolas), comprised of two hydrophilic head groups connected by one or two long hydrophobic spacers, can be used to synthesize PEG-bolas to improve the bilayer retention ability. Bolas predominantly adopt a membrane-spanning configuration that confers robust bilayer retention. Therefore, a series of sugar-based PEG-bolas that build upon bola architecture were developed, comprised of PEG as hydrophilic head groups and acylated tartaric acid as hydrophobic building block. Our hypothesis was that PEG-bolas with a sufficiently long hydrophobic domain could preferentially extend across lipid bilayers, leading to improved bilayer retention and subsequent enhanced integrity of PEG protective layer. PEG-bola chemical structures were confirmed by nuclear magnetic resonance spectroscopy and gel permeation chromatography. The liposomal retention ability and stability were evaluated in comparison to PEG-lipids. These studies indicated PEG-bolas demonstrated significantly enhanced retention in liposomes, resulting in improved colloidal and biological stability of liposome formulations.

**Designing a targeted photodynamic therapy against triple negative breast cancer**

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In the United States (US) alone, breast cancer is the most common cancer affecting women, and the second leading cause of cancer-related deaths among women. In 2015, around 231,840 new cases of invasive breast cancer are likely to be diagnosed
among women and 2,350 new cases for men in the US. About 10-20% of all breast cancer cases are further classified as triple-negative breast cancer (TNBC) where the cells are lacking estrogen, progesterone and Hormone Epidermal Growth Factor Receptor 2 (HER2) receptors on the cell surface; hence, hormone or HER2 targeted therapies are not viable treatment options. Chemotherapy is often used as an alternative method, yet conventional chemotherapy drugs have very high toxicity due to lack of selectivity leading to poor quality of life among TNBC patients. Nanoparticle-based drug delivery can overcome these limitations by targeted delivery of the chemotherapy drugs. Using remotely-triggered methods of inducing toxicity in the cancerous tissues could further enhance the selectivity of treatment and limit collateral damage to healthy tissues. This research aims to overcome the limitation of selectivity in TNBC therapy by using targeted nanoparticles that are loaded with a photodynamic agent, chlorin E6 (cE6). This non-toxic drug can be used as a dye in fluorescence imaging and as a photosensitizer for the treatment of TNBC when activated by light via photodynamic therapy (PDT). The nanocarriers synthesized in this study are folate conjugated liposomes which encapsulate cE6. The conjugation of folate enhances the targeting capability of the liposomes to cancer cells which over-express folate receptors (FRs) on their cell surface. The experiment began with the encapsulation of cE6 by FA-conjugated-liposome and the particles were extruded through a 100nm filter membrane. The resulting liposomes were characterized for their size and zeta potential using Dynamic Light Scattering instrument (DLS), and the cE6 absorbance level to determine encapsulation efficiency of cE6 in the liposome via ultraviolet-visible spectroscopy (UV-Vis). The cE6/liposome complex uptake was tested on MDA-MB-231 cells and observed using fluorescence microscopy. The final step of the study was to test the efficiency of the nanodrugs using PDT treatment on MDA-MB-231 cells as cE6 are known to be an effective photodynamic agent. Results of this study will be presented.

COLL 197

Controlling hydrosilylated pin-printed feature sizes on porous silicon

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Porous silicon (pSi) is an ideal candidate for optical sensing due to its characteristic photoluminescence, large surface area, ability to be integrated into existing silicon technologies, and surface silane (Si-Hₓ) groups readily available for functionalization. High density microarrays on pSi platforms will allow for multi-analyte sensing simultaneously within a relatively small analysis area which is optimal for detection using optical microscopy. A significant issue with robotic pin-printing on pSi is feature spreading, limiting arrays to low feature densities over large surface areas. A 3 x 1 and 3 x 3 array of 1-octadecene features were pin-printed and hydrosilylated onto pSi platforms of different porosities and surface polarities, respectively, to optimize array density. pSi porosity was controlled using different anodization times and surface polarity was adjusted by H₂O₂ oxidation. The pin-printed and hydrosilylated feature
dimensions were characterized by infrared (IR) spectroscopy for the x,y-directions and x-ray photoelectron spectroscopy (XPS) depth profiling for the z-direction. Pin-printed and hydrosilylated 1-octadecene feature diameters decreased by 70% with increasing pSi porosity from 26 to 75%. pSi surface polarity differences, measured through IR spectroscopy and contact angle, had no observable effect on resulting feature size suggesting that pSi porosity is the controlling factor in feature size spreading. 1-Octadecene penetrated the pSi layer 0.50, 0.87, 0.99, and 1.5 μm for the 30, 60, 150, and 300 s pSi anodization times, respectively, suggesting that 1-octadecene depth penetration is limited by pSi porosity and thickness. Other factors, such as reagent viscosity and pin diameter, were also explored to control feature spreading. pSi porosity, alkene viscosity, and pin diameter are the most effective ways to optimize microarray density on pSi.

Effect of porosity (anodization time) on pin-printed 1-octadecene feature diameters. (pSi nanocrystallites not drawn to scale).

COLL 198

Surface properties of xerogel materials with unusual patterns and tunable topography for antifouling applications

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Over the past decade, research from our laboratories has focused on developing organically-modified hybrid xerogel coatings that exhibit antifouling and fouling-release characteristics. Hybrid Si-based xerogels are of interest because they are readily prepared by the sol-gel process and they form films which can be covalently bonded to naturally stable metal oxide surfaces. Furthermore, xerogel chemistry and topography can be conveniently adjusted by controlling substitution at the –R’ group on the (OR)₃Si–R’ precursor(s) and the precursor molar ratios; allowing for design flexibility. Here we report the fabrication and characterization of a hybrid xerogel coating composed of carboxyethyltriol silane (COE) and tetraethoxysilane (TEOS). These coatings exhibit an interesting hierarchical snowflake or fern-like surface pattern which is shown to be compositionally dependent. Topographic and morphological properties of the films were assessed by atomic force microscopy (AFM), scanning Kelvin probe microscopy (SKPM) and scanning electron microscopy (SEM). Chemical properties were assessed by confocal Raman mapping. In addition, a novel method for assessing the local acidity/basicity was also developed, using fluorescence multispectral imaging and a ratiometric pH probe.

Measured surface topography and local pH of a typical COE-TEOS coating.
Aerosol-based ultrasonic synthesis of polymer-conjugated metallic nanobunches to fabricate transparent antimicrobial layers

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Polymer-conjugated metallic nanoparticles were continuously obtained in a single-pass configuration by appropriately reacting freshly aerosol-synthesized metal particles with another metallic particle formed in an ultrasonic aqueous medium containing polymer. The synthesized nanoparticles were employed as inducers for the antimicrobial actions at different conditions. Aerosol-synthesized metal particles were quantitatively incorporated with another particle containing polymer in the form of polymer-conjugated metallic nanocomposites via a successive ultrasonic reaction and electrospray process. Measurements of the nanoparticle cytotoxicity revealed that polymer incorporation with metallic particles significantly decreased the cytotoxicity of metal. The nanocomposites were directly coated on to a substrate through an electrospray device to fabricate transparent layers. The antimicrobial layers were further employed to evaluate their antimicrobial activity.

Carbon nanotube scaffolded self organized silica gels

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It is well known that by controlling self-assembly of the templating agents, aspects such as elasticity, macro and micro scale structure, and transparency of the resulting materials can be tailored [1]. However, experimental science in this area of research is in it’s infancy in comparison to nature’s intricate assemblies, which have evolved over the millions of years to develop such control. We have been interested in employing carbon nanotubes as templates for attaching polymers, due to their rigidity and small size [2]. Provided these nanotubes remain interconnected, electrical conductivity can be controlled via altering percolation [3].

In this paper, we present a novel facile synthetic strategy for generating metal nanoparticle impregnated silyl based sol-gels with carbon nanotube scaffolding. Various silanes were studied for their ability to reduce and complex metal nanoparticles and control of self-assembly. Silylated compounds provide a unique aspect of study for their ability to hydrolyze forming crosslinked silica matrices. Through hydrolysis of silanes, we can generate a silica matrix containing noble metal nanoparticles. We covalently graft these nanocomposites onto functionalized carbon nanotubes to act as scaffolding. Analysis of these materials was conducted with TEM, SEM/EDS, and UV-Vis spectrometry.


COLL 201

Catalytic investigations of hybrid metallic nanoparticle nanogels: The effect of silylation on self assembly and activity

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Hybrid nanocomposites are materials that are created by incorporation of at least two different components, each of which provide unique properties to the resulting product. In particular, nanogels embedded with metallic nanoparticles are valuable hybrid materials not only in drug delivery therapeutics and medical imaging, but also other industrial applications such as large-scale catalysis. If the hybrids are created by carefully selected functionalities, they can be rendered highly tunable in terms of chemical reactivity. Studies in our group as well as by others have shown that nanogels impregnated with metallic nanoparticles provide a hybrid system, where one has unique optical, mechanical, and electrical properties of the colloidal metal nanoparticles within
the physiochemical structure of the nanogel [1].

In our previous work, we characterized the different properties of metallic nanoparticles synthesized by a well-documented polymer, polyethylenimine versus its silyl-substituted version, trimethoxysilylpropyl-polyethylenimine. Both systems exhibited a distinct difference in nanoparticle sizes, morphologies, and therefore applications [2]. In this work, this highly tunable system was chemically cross-linked using silanes, such as triethoxysilane (TES) and tetraethoxysilane (TEOS) to produce a nanogel. The resulting products were characterized via FT-IR, TEM, SEM, TGA, and AFM. These nanogels were then assessed for their catalytic activity for reduction reactions of nitrophenol. The comparative catalytic studies were carried out under identical molar ratio's and reaction conditions. The catalysts were also assessed for their recyclability properties. A comparative analysis to their colloidal counterparts was also undertaken. Future studies of their toxicity and target-selectivity via cell studies are underway in our laboratory.


COLL 202

SIRB, Sans Iron Oxide Rhodamine B, a novel cross linked dextran nanoparticle

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This is the first report of the synthesis of a new nanoparticle, Sans Iron Oxide Rhodamine B (SIRB), an example of a new class of nanoparticles, Sans Iron Oxide Nanoparticles (SION). SIRB is a nanoparticle designed to provide all of the cell labeling properties of the Ultrasmall Superparamagnetic Iron Oxide nanoparticle (USPIO), Molday ION Rhodamine B (MIRB). MIRB was developed to label cells and allow them to be tracked by MRI or manipulated in vitro or in vivo by magnetic gradients. SIRB possesses a similar size, charge and cross-linked dextran coating as MIRB (Table 1). Removing MIRB’s iron oxide core produces the new nanoparticle, SIRB) that we call (by analogy with the terminology used to name red cell ghosts) a USPIO ghost. The approach to synthesizing SIRB can be applied, in principle, to all cross-linked USPIOs. Examples of cell labeling with SIRB along with its toxicity profile are presented in a companion abstract.
Table 1. Comparison of fluorescence, and hydrodynamic properties and iron concentration of MIRB and SIRB.

<table>
<thead>
<tr>
<th></th>
<th>MIRB</th>
<th>SIRB</th>
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</thead>
<tbody>
<tr>
<td><strong>Fluorescence</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ex-max (nm)</td>
<td>560.8</td>
<td>559.6</td>
</tr>
<tr>
<td>Em-max (nm)</td>
<td>581.4</td>
<td>579.6</td>
</tr>
<tr>
<td><strong>Size (nm)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>48.0±6.4</td>
<td>47.8±3.1</td>
</tr>
<tr>
<td>PBS</td>
<td>44.4±4.7</td>
<td>41.5±3.1</td>
</tr>
<tr>
<td><strong>Zeta Potential (mV)</strong></td>
<td>+14.5±5.6</td>
<td>+13.3±5.7</td>
</tr>
<tr>
<td>Fe (mg/ml)</td>
<td>2.0</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

*The size (5 determinations) and zeta potential (10 determinations) of MIRB and SIRB are presented as mean and standard deviation. Means and zeta potential of MIRB and SIRB were tested for significance using a two tailed Student t-test. None of the matched pairs were considered to be statistically different. Fluorescence was a single determination. Iron concentration for MIRB represents a manufacturing target which has been maintained over 20 manufacturing runs. Iron concentration was determined on three preparations of SIRB.

**COLL 203**

**SIRB**, Sans Iron Oxide Rhodamine B, a novel crosslinked dextran nanoparticle, labels human neuroprogenitor and SH-SY5Y neuroblastoma cells and serves as a USPIO cell labeling control nanoparticle

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USPIOs (ultrasmall superparamagnetic iron oxide nanoparticles) are used in preclinical research as MRI contrast agents, drug delivery vehicles and stem cell labeling reagents. Of great interest is understanding the biological and physiological changes in cells after they are labeled by USPIOs. Whether these labeling effects are due to the iron oxide buried within the nanoparticle or to the surface coating surrounding the iron oxide core has not been considered previously. To address this general question, we have used a
new nanoparticle undergoing preclinical development (SIRB). SIRB\(^1\) is similar to the crosslinked dextran coated iron oxide nanoparticle MIRB (Molday ION Rhodamine B)\(^2\) in all respects except that it contains no iron oxide. MIRB and SIRB, therefore, represent an ideal pairing of nanoparticles to identify nanoparticle anatomy responsible for post-labeling cytotoxicity. Here we report on the effects of SIRB labeling on the SH-SY5Y neuroblastoma cell line and primary human neuroprogenitor cells (hNPCs).

These effects are contrasted with the effects of labeling SH-SY5Y and hNPC cells with MIRB, the iron oxide loaded twin nanoparticle of SIRB (Table 1). We find that SIRB labeling, like MIRB labeling (i) occurs without the use of transfection reagents; (ii) is packaged within lysosomes uniformly distributed in the cell’s cytoplasm; (iii) is retained within cells with no loss of fluorescent label after cell freezing, storage, thawing and replating; (iv) does not alter cellular viability or proliferation of hNPC and SH-SY5Y cells; and (v) SIRB labeled hNPCs differentiate into neurons or astrocytes, just as unlabeled hNPCs. Our comparison points to the importance of using control nanoparticles as well as USPIOs to label stem cells.

1. The synthesis of SIRB is described in our companion abstract.
Table 1. Comparison of hNPC or SH-SY5Y cells labeled with MIRB or SIRB.

<table>
<thead>
<tr>
<th></th>
<th>MIRB</th>
<th>SIRB</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cells Labeled</td>
<td>98.0 + 2.0</td>
<td>99.3 + 0.4</td>
</tr>
<tr>
<td>SH-SY5Y</td>
<td>98.2 + 1.8</td>
<td>93.2 + 1.4</td>
</tr>
<tr>
<td>hNPCs Undifferentiated</td>
<td>95.4 + 2.4</td>
<td>97.0 + 1.2</td>
</tr>
<tr>
<td>% Cell Viability Following Labeling</td>
<td>94.0 + 1.3</td>
<td>94.8 + 1.9</td>
</tr>
<tr>
<td>SH-SY5Y</td>
<td>92.8 + 2.6</td>
<td>92.7 + 2.7</td>
</tr>
<tr>
<td>hNPCs Undifferentiated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transfection agent</td>
<td>Not required</td>
<td>Not required</td>
</tr>
<tr>
<td>Proliferation (BrdU incorporation)</td>
<td>Unchanged with respect to unlabeled cells</td>
<td>Unchanged with respect to unlabeled cells</td>
</tr>
<tr>
<td>Cryogenic storage</td>
<td>MIRB Retained</td>
<td>SIRB Retained</td>
</tr>
<tr>
<td>During hNPC differentiation</td>
<td>MIRB Retained</td>
<td>SIRB Retained</td>
</tr>
<tr>
<td>Intracellular distribution</td>
<td>Lysosomes</td>
<td>Lysosomes</td>
</tr>
</tbody>
</table>

COLL 204

Novel plasmonic platform for label-free biosensing with membrane-associated species

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Supported lipid bilayers have become essential model systems for studying membrane proteins and the behavior of lipid bilayers. Incorporation of metal nanoparticles that host localized surface plasmon resonances (LSPRs) with biocompatible surfaces is an attractive method for developing label-free, refractive index based sensing schemes. In order to effectively expand the applicability of noble metal nanoparticles to membrane systems, highly sensitive nanoparticle arrays combined with biocompatible interfaces are needed. To this end, surface-bound nanoparticles prepared through hole-mask colloidal lithography have been encapsulated in silica to create embedded LSPR sensor elements. These novel platforms allow for facile preparation of surfaces with controllable composition that are amenable to lipid adsorption. Increasing nanoparticle
size and concomitantly shifting the LSPR to near-infra red wavelengths is found to dramatically increase the sensitivity of these substrates. Adsorption of phospholipids, protein binding, and lipid mobility is demonstrated and monitored by shifts in LSPR frequency and fluorescence recovery after photobleaching (FRAP). In addition, structural characterization and optimization of the samples is carried out using both atomic force microscopy (AFM) and scanning electron microscopy (SEM).

**COLL 205**

**Eco-friendly scratch resistant wood coatings based on silica nanoparticles**

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Waterborne polyurethane dispersions (WPU) produced via acetone process present a feasible and eco-friendly alternative to commercial solvent-based coatings. The amount of volatile organic compounds (VOC) can be completely reduced with responsibility to the state of health. However, WPUs have the major disadvantage of low scratch resistance due to their film formation mechanism. To increase the scratch resistance, organic modified silica nanoparticles were combined with aqueous polyurethane particles. Monodisperse silica nanoparticles were produced via the well-known stoeber process and were further functionalized with amines, thiols or isocyanates. These were directly introduced into the WPU process to obtain an inorganic/organic hybrid material. This results in a covalent bonding between PU and silica particles to ensure a homogeneous particle dispersion. After film formation the inorganic compounds were homogeneously distributed in the PU matrix increasing the scratch resistance. The difference compared to commonly used pyrogenic silica is the well-defined spherical shape with an average diameter under 100 nm. With this method the amount of silica can be increased up to 20 wt%. In addition, there is no loss of transparency in the resulting film. The WPU process proves to be an elegant way to disperse a large variety of functionalized nanoparticles in a spreadable matrix important for wood coatings. With this approach, silica-based raspberry particles were embedded in a PU film leading to highly hydrophobic scratch-resistant coatings.

**COLL 206**

**Promotion of the halide effect in the formation of metal nanocrystals via a hybrid cationic, polymeric stabilizer: Octahedra, cubes, and anisotropic growth**

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To promote the effect of halide ions in the growth of shaped Pd nanocrystals, we utilize polydiallyldimethylammonium halides (PDADMAX, X = halide), a hybrid cationic,
polymeric stabilizer. Surface enhanced Raman spectroscopy (SERS) and synthesis experiments provide evidence supporting the high concentration of PDADMA\(^+\) on metal surfaces promotes the local surface adsorption of halides and enhances their selectivity in facet-capping. By utilizing the preferences of Cl\(^-\), Br\(^-\), and I\(^-\), in binding of Pd \{111\} and \{100\} atomic planes in this system, we confirm the role of halides in directing shape-controlled growth and demonstrate the creation of Pd cubes, Pd octahedra, and novel, Pd cuboctopods (a portmanteau between ‘cuboctahedra’ and ‘octopod’) by simply tuning the halides. Notably, the new cuboctopod morphology’s TEM cross-section resembles the auspicious four-leaf clover, and can be used to deduce the anisotropic growth mechanism, where the eight uncapped high-energy vertices of the substrate cube serve as seeding sites for epitaxial overgrowth in the \(\langle111\rangle\) direction in a two-step method. The information gained here was then extended to the Pt system, where Pt cuboctopods could be produced in a one-step reaction. We believe the critical roles of this unconventional stabilizer in producing shaped Pd and Pt nanocrystals can be used to further push the boundaries of metal nanoparticle synthesis, where better shape-control at smaller sizes is desired for heterogeneous catalysis. This method also shows promise for applications in electrochemical catalysis, where PDADMAX can serve dual roles as both nanoparticle stabilizer and polymer electrolyte.

**COLL 207**

**Chlorinated protein films for antimicrobial coatings**

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Antimicrobial films are important for wound healing, medical devices and food industry. Chlorinated films have antimicrobial efficacies similar to that of hypochlorite bleach, but they are more stable and less corrosive. Current approaches for generating chlorinated films requires the synthesis of special motifs within polymers for chlorination. Here, we report a simple and eco-friendly strategy for generating protein film by nanoimprint lithography (NIL), serving as a scaffold for chlorination. Protein-based films are inherently biocompatible and biodegradable. After the NIL process, the protein films were stable in aqueous solution, and resisted to bacteria adhesion. The diversity of amino acids on protein building blocks enables the post-functionalization. After chlorinating by sodium dichloroisocyanurate, the protein films showed strong biocidal activity, inhibiting bacterial growth via the slow release of chlorine. This strategy uses natural abundant biomaterials as precursors, requires no synthetic expertise, works under aqueous conditions, and is eligible for roll-to-roll processing, which is promising for large-scale antimicrobial coating fabrication.
Protein film fabricated through nanoimprint lithography (NIL) serves as a stable scaffold that prevents bacteria adhesion. After chlorination, the protein film can release chlorine and kill bacteria in solution.

**COLL 208**

*National synchrotron X-ray scattering facility dedicated for the studies of molecular ordering and dynamics at liquid surface/interfaces*

*Wei Bu, weibu1977@gmail.com, Binhua Lin, Mati Meron. University of Chicago, Argonne, Illinois, United States*

A liquid surface/interface spectrometer has been commissioned successfully since the summer of 2002 at the ChemMatCARS national synchrotron user facility (15-ID) at the Advanced Photon Source (Argonne National Laboratory). The spectrometer was designed and developed for the investigation of interfacial phenomena and properties of a wide variety of liquid systems, such as, environmental chemistry at liquid interfaces, chemistry of life processes and biomolecular materials, and directed assembly for tailored functionality at liquid interfaces. The high brilliance and wide X-ray energy range (5-70keV) offered in this third generation insertion device beamline provides a world-leading capability for the study of liquid surfaces and buried liquid-liquid interfaces. A full suite of x-ray surface scattering techniques is provided to measure atomic, molecular, and mesoscopic ordering at liquid interfaces, including resonant and non-resonant reflectivity, grazing-incidence diffraction and small angle scattering, surface fluorescence, surface diffuse scattering, and fast techniques, such as grazing incidence diffraction in the 1D pinhole geometry. In this poster we present a brief introduction of this facility and some recent research highlights from general users.

**COLL 209**

*Histamine-functionalized copolymer micelles as a drug delivery system in 2D and 3D models of breast cancer*
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Polymer based nanoparticles (NPs) has been widely investigated as drug delivery systems (DDS) during the last decade. One major challenge for effective drug delivery using NPs is to evade endosomal/lysosomal entrapment and relocate the drug into the cytoplasm. One strategy is to design pH responsive polymers that can be charged under acid environment and escape from endo/lysosomes via the ‘proton sponge’ effect.

In this research, a comprehensive library of polymer micelles based on poly(allyl glycidyl ether)-b-poly(ethylene oxide) (PAGE-b-PEO) were developed using UV initiated thiol-ene click chemistry to graft different amounts of histamine, and octane or benzyl groups to enable a pH sensitive property to the block copolymer. The histamine groups are uncharged and hydrophobic at neutral pH, while they can become positively charged and transform to hydrophilic when encountering an acidic environment (Lundberg et al. Soft Matter, 2013), such as in the endosome, lysosomes, or extracellular sites of tumors.

To evaluate these polymer NPs as DDS, we established 2D and 3D cultures models of breast cancer cells (MDA-MB-231) to investigate the NP composition effect on toxicity and cargo distribution. The efficacy assays revealed that DOX-NPs demonstrated significant stronger efficacy in short time (12-24 h) treatment compared to free DOX. And the NPs with 50% histamine functionalization showed the strongest efficacy compared to other NPs under longer treatment (72h). Further intracellular tracking of DOX-NPs in 2D models displayed that DOX from the 50% histamine functionalized NPs could accumulate in the nuclei rapidly (within 2h). Moreover, an enhanced co-localization of this DOX-NPs to mitochondria was observed while weaker signals were found in endosomes and lysosomes compared to free drug and other DOX-NPs. These results suggested that the 50% histamine containing NPs could partly escape from endo/lysosomal entrapment and relocate DOX into the nuclei and mitochondria. These results were further confirmed in 3D models showing that 50% histamine containing NPs, especially the one from the low histamine /low PEG molecular weight group is the most promising carrier for drug delivery applications.

From these combined studies, we can conclude that by tuning the chemical composition, the consequent NPs can be designed to employ histamine as an endo/lysosomal escape trigger and achieve improved drug delivery efficacy by tailoring its intracellular distribution.
Trace amounts of metals in food and consumer products catalyze oxidation reactions that decrease quality and shelf life of packaged foods. Traditionally, synthetic metal chelators, such as ethylenediaminetetraacetic acid (EDTA), are added to stabilize these products. Due to consumer demand for 'clean' labels, there is increasing interest in alternative preservation methods. One such method is metal chelating active packaging. We have previously synthesized novel metal chelating active packaging materials that inhibited oxidation in oil-in-water emulsions and have demonstrated that their efficacy is dependent on the chelator chemistry (iron affinity, pKa). Plant-derived phenolic compounds that contain catechols are reported to have high affinity for iron (e.g. catechol log β_{Fe(III)} = 43.76, catechin log β_{Fe(III)} = 47.4)\(^1\) and potent surface adhesion properties after polymerization. The objective of this study was to synthesize a novel polyphenol coating for development of metal chelating active packaging materials. Polyphenol coatings were applied to the surface of polypropylene by in situ polymerization of a mixture of catechol and catechin (2.5 mg/ml catechol; 2.5 mg/ml catechin) via enzymatic polymerization with laccase (1 mg/ml in 100 mM sodium acetate buffer pH 5 and methanol (9:1)) or oxidative polymerization in buffered saline (100 mM bicine, 600 mM sodium chloride pH 8). Polyphenol coated materials were characterized by colorimetry, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), Folin Ciocalteu assay, and iron chelating assay. Coated materials had a dark brown color and exhibited ATR-FTIR absorbance bands that demonstrated successful deposition of polyphenol coating. Laccase-catalyzed polyphenol coatings contained 86.7 ± 12 nmol catechol eqv. cm\(^{-2}\) and buffered saline polyphenol coatings contained 33.1 ± 7.3 nmol catechol eqv. cm\(^{-2}\). For both polyphenol coatings, optimum iron chelation was demonstrated at pH 4 (ie: laccase-catalyzed coating 51.3 ± 4.7 nmol Fe\(^{3+}\) cm\(^{-2}\), buffered saline coating 41.7 ± 6.6 nmol Fe\(^{3+}\) cm\(^{-2}\). Dual functionality of catechol containing polyphenol coatings as potent chelators and anchors makes them a promising candidate for application in active packaging that can inhibit metal-promoted oxidative degradation.


**COLL 211**

*Phospholipid/aromatic thiol hybrid bilayers*
Gold-supported hybrid bilayers comprising phospholipids and alkanethiols have been found highly useful in biomembrane mimicking as well as biosensing ever since its introduction by Plant in 1993 (Langmuir, 1993, 2764-2767). Generalizing the mechanism (i.e., hydrophobic/hydrophobic interaction) that primarily drives the bilayer formation, we report here that such a bilayer structure can also be successfully obtained when aromatic thiols are employed in place of alkanethiols. Four aromatic thiols were studied here: thiophenol, 2-naphthalene thiol, biphenyl-4-thiol, and diphenylenevinylene methanethiol, all affording reliable bilayer formation when 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine liposomes were incubated with self-assembled monolayers of these thiols. Characterization of the resultant structures, using cyclic voltammetry, impedance analysis and atomic force microscopy, confirms the bilayer formation. Significant differences in electrochemical blocking and mechanical characteristics of these new bilayers were identified in comparison to their alkanethiol counterparts. Taking advantage of these new features, finally, we present a new scheme for straightforward detection of a lipolytic enzyme (phospholipase A2) using these phospholipid/aromatic thiol bilayers.

All-lipid assembled photosynthetic mimics

We present here a new photosynthetic mimicking strategy that relies on supercomplexed lipid nanoassemblies to organize small organic species for coordinated light harvesting, energy/electron transfer and photo-to-electrochemical energy conversion. Specifically, we demonstrate that efficient photoinduced electron transfer can be achieved between rhodamine and fullerene assembled in these nanoassemblies. The remarkable possibility of using lipid matrix to improve photoconversion efficiency is further revealed by cholesterol, whose addition triggers exciton formation that leads to faster energy transfer in these lipid nanoassemblies. The architecture, photodynamics and photoelectrochemical behavior of these lipid complexes were characterized and evaluated in the context of building protein-free photosynthetic mimics.
The combination of electroless gold plating and photocontrolled molecular film formation by hydrosilylation of 1-alkenes on silicon nitride—an important nanofabrication material—has paved the way for an inexpensive, robust and reproducible photo-controlled gold patterning technique. The molecular layers covalently linked to silicon nitride form a barrier mediating the interaction of solution-phase metal ion-containing species with the silicon nitride surface, thereby allowing us to tune the propensity of electroless plating to occur on the organic layer versus the silicon nitride layer. By selection of appropriate 1-alkenes, we have selectively plated thin (<100nm) gold features. Owing to their nanostructure, the gold films are effective substrates for surface-enhanced Raman spectroscopy (SERS). Raman signal strength can be tuned by controlling the gold nanostructure by modifying the plating conditions or by careful choice of the molecular layers synthesized on silicon nitride. We explored the latter effect by using chemical synthesis to modify the terminal group of a photoattached organic layer. Beneficial chemical modifications yielded clear enhancements of the SERS signal, and complementary characterization by scanning electron micrographs revealed compelling changes to the film nanostructure.

**COLL 214**

**Electroless plating of thin gold films directly onto silicon nitride thin films and into micro- and nanopores**

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Single molecule studies depend upon precise control over the chemical and physical structure of the nanoscale sensing instrumentation and environment, and this demand is particularly stringent in the case of nanopores, a unique tool for single-molecule sensing and manipulation. The size and shape of the nanopores are critical to their function, and each facet, alone, presents experimental hurdles; this work contains an approach to address both, simultaneously. A method for electroless deposition of gold onto solid-state silicon nitride nanopores provides a foundation for precision tailoring of surface properties and nanopore size to study single analyte molecules and their interactions with other molecules of interest. This work has developed a set of tools to directly modify the surface of silicon nitride, and through this approach, to customize the nanopore size and surface properties for various molecular systems under investigation.
COLL 215

Molecular layers on nanoporous gold electrodes

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Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium salts to create aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method.

COLL 216

Rapid, electroless surface modification through surface-directed azo coupling

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Grafting of aryl diazonium salts by spontaneous or reductive decomposition is a widely used technique for producing functionalized thin films. The technique is useful due to its simplicity and the robustness of the layers produced, but is difficult to control and the rapid reductive method is limited by the need for an external potential or reducing agent. We present an alternative method for grafting aryl diazonium salts to a surface by reacting diazonium ions in solution with an electron-rich aromatic monolayer in a classical azo or Gomberg coupling. This method combines the rapidity of reductive electrografting with the controllable nature of self-assembly, and yields a photoswitchable layer due to the azobenzene moiety in the product. The resulting layers have been studied by voltammetry and IR spectroscopy, and their switchability characterized by electrochemical impedance spectroscopy and contact-angle measurements.
Electrospun polytetrafluoroethylene thin film with high heat transfer coefficient

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Heat transfer by water condensation is used in factories, power plants and so on (Figure 1a). Although the previous studies have focused on the enhancement mechanism of heat transfer by condensation for efficient use of energy and cutting cost, it has not been grasped in its entirety, especially a correlation between surface wettability and heat transfer coefficient. There are two types of condensation, filmwise condensation and dropwise condensation. The filmwise and the dropwise condensation form water thin film and droplet on the surface, respectively, and the dropwise condensation shows higher heat transfer coefficient than the filmwise condensation. However, there are no unified theories on relationships between wettability and heat transfer coefficient at dropwise condensation. Therefore, we fabricated surfaces with different wettability by using PTFE which can endure high temperature environment, then constructed heat transfer condensation system, and lastly measured heat transfer coefficient. We mixed PTFE and Polyvinyl alcohol (PVA) as solutions and electrospun them on Al tubes (Figure 1b). After electrospinning, we annealed surfaces at 370°C to vaporize PVA and harden PTFE. We changed the wettability by changing tip to collector distance (TCD) and mixing ratio of PTFE and PVA. Longer TCD and decrease of mixing ratio led to decrease of contact angle because roughness was decreased. After that, we gained results of heat transfer coefficient (Figure 2a). From the mechanism of heat transfer (Figure 2b), the smaller max droplet diameter and high departure frequency of droplets are, the better for heat transfer. However, no surfaces filled those two conditions at the same time. Therefore, we concluded that the surface that contact angle was 85° showed the highest heat transfer coefficient because the combination of max droplet diameter and departure frequency of droplets led to the smallest thermal resistance.
Figure 1. (a) The model of heat transfer by water condensation (b) SEM image of electrospun Al tube surface

(a)  

Figure 2. (a) Contact angle vs. Heat transfer coefficient (b) The mechanism of heat transfer

COLL 218

Toward the synthesis of ordered mesoporous organosilicas with closed mesopores

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Ordered mesoporous organosilicas with different organic groups were synthesized using Pluronic F127 surfactant as a templating agent. The organic groups were selected on the basis of their facile thermal stability. The organosilicas had pore diameters around 10 nm and periodic arrangements of mesopores. The feasibility of converting the ordered mesoporous organosilicas to closed-pore materials through the thermal treatment was investigated with the goal of closing the mesopores without any cleavage (or with minor cleavage) of the organic groups. The materials were characterized using nitrogen adsorption, small-angle X-ray scattering, transmission electron microscopy, $^{29}$Si and $^{13}$C MAS solid state NMR. Our work shows the challenges and opportunities in achieving the closed-pore organosilica structures through the thermally induced pore closure process.

COLL 219

KillerRed conjugated upconversion nanoparticles for cancer imaging and photodynamic therapy
Photodynamic therapy (PDT) is a highly specific and minimally invasive anti-cancer treatment modality for various cancers. Use of upconversion nanoparticles (UCNPs) in PDT as transducer and nanoplatform has received much attention in recent years. Owing to their unique optical properties, UCNPs are able to convert the near-infrared excitation light to high-energy visible light and activate the surrounding photosensitizers (PS) to generate singlet oxygen or other reactive oxygen species (ROS) and kill cancer cells. Different from the traditional visible or UV excitation PDT strategies, NIR-excited PDT based on UCNPs can be used in much deeper tissues and realize simultaneous imaging and therapy by employing PS in the nanoplatforms.

In this work, we report a novel photosensitizing nanoplatform for cancer fluorescence imaging and photodynamic therapy by conjugating KillerRed to UCNPs. KillerRed has been proven to produce ROS under light exposure to initial cell death. Green emission from UCNPs at around 545 nm overlap the excitation of KillerRed, therefore UCNPs can activate the attached KillerRed to produce ROS via resonance energy transfer. It is believed that the biocomplex UCNPs-KillerRed has upconversion luminescence and PDT ability which could be used as a theranostic platform for cancer imaging and treatment.
Dynamic coupling at the Ångström scale

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We measure the momentum distribution around angstrom scale molecular swimmers through a series of experiments using diffusion (DOSY) NMR spectroscopy. Momentum transfer from active catalysts to their surroundings has previously been reported for colloidal systems involving micro- and nanoscale particles. Our observations show that such processes can occur even at lower Reynolds number systems, significantly influencing the dynamics of the entire system. Diffusion of both tetramethylsilane and benzene dispersed in a solution of Grubbs’ second generation catalyst undergoing a ring closing metathesis reaction is enhanced in the presence of catalysis. The enhancements are characterized as functions of time and total rate of reaction in the system. We hypothesize that the enhancement in tracer motion is due both to reaction-generated convection and hydrodynamic coupling among the molecules. The results show that localized energy transduction in active suspensions can incisively alter the dynamics of a fluidic system, offering tremendous scopes for advancing frontiers of small scale mixing, assembly and delivery of materials.
viscosity. As total reaction rate increases the diffusion of the tracers is enhanced significantly, thereby displaying increased momentum transfer from the active catalysts to their surroundings. Units of reaction rate are moles of substrate consumed per mole of the catalyst, per second.

**COLL 221**

**Enhanced cell performance with control of ZnO buffer layer using nanoparticles of various morphology for inverted organic photovoltaic cells (OPVs)**

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Zinc oxide (ZnO) had been applied in OPVs as electron transfer layer because it had wide band gap energy (3.37 eV) and large exciton binding energy (60 meV). In this study, we have controlled the morphology of ZnO nanoparticles for improvement of cell performance in OPVs. Four type of ZnO nanoparticles were prepared for investigation of cell efficiency. The prepared samples, which were fabricated by using spherical particles, rod-shape particles, mixture of sphere/rod particles, and bi-layer of sphere/rod particles were identified as SZ, RZ, MZ, and BZ, respectively. The performance of device fabricated with MZ was higher than other devices due to the flat surface particles behaved as an easy channel to get better the current density (Jsc). The degree of surface roughness can be found by AFM analysis and the IPCE analysis revealed that the device converts the incident light into electrical energy at a given wavelength. In case the MZ, the best device exhibits a power conversion efficiency (PCE) of 2.75 % under 100mW/cm-2 at AM 1.5 G simulated solar emission.

**COLL 222**

**Silver sulfadiazine-immobilized inorganic fillers: Preparation, characterization, and antimicrobial functions**

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In the present study, we developed a new strategy to covalently attach silver sulfadiazine, a widely used antimicrobial agent, onto the surfaces of inorganic fillers to achieve antimicrobial effects. In our approach, barium borosilicate based glass powder (average particle size 0.7 µm) was functionalized to introduce amino functional groups onto the surfaces. Cyanuric chloride was used as a bridging agent to covalently bond sulfadiazine onto the amino groups. The resulting glass powders were treated with silver nitrate aqueous solutions to transform the sulfadiazine moieties into sulfadiazine-silver coordination complexes. The chemical structures of the new glass fillers were fully characterized, and the antimicrobial effects were demonstrated with zone of inhibition studies.

The antimicrobial modified glass powders can be used in various biomedical
applications. One of such potential applications is antimicrobial dental restorative materials to control secondary caries. These restorative dental composite resins are mainly composed of acrylic monomer resins along with inorganic fillers. To test the suitability of the new glass powders for this application, a series of different resin composite formulations were prepared by replacing part of the inorganic fillers with this silver sulfadiazine immobilized glass powders. The resulting composites showed potent antimicrobial effects, pointing to great potentials for real applications.

COLL 223

Removal of oxidation debris from carboxylated carbon nanotubes

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Oxidation debris are generated during oxidation and carboxylation of carbon nanotubes, which is usually the first step in their functionalization. Dilute base-washing has been shown to remove oxidation debris by converting the acidic groups to their dissolvable conjugate salts. In this research we present the effect of base-washing of microwave induced carboxylated carbon nanotubes (CNTs). The carbon to oxygen ratio, the BET surface area, the ratio of D–G bands based on Raman measurements as well as the solubility changed with base wash. However, zeta potential and particle size showed no significant alterations with the wash. Toxicity measurements and IL-1b release from the THP-1 cells in the presence of CNTs also showed no alteration with base wash. The analysis of the wash showed the presence of graphitic carbon but the absence of small CNT fragments. These results demonstrated that the oxidation under microwave conditions generated relatively less debris and fragmentation, and this is a good approach to acid functionalization of CNTs.

COLL 224

Characterization of carbon nanotube composites by imaging X-ray photoelectron spectroscopy: Employing differential charging to detect carbon in carbon

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Carbon nanotubes CNTs are commonly used to enhance many polymeric materials in the formation of composites due to the desirable properties they can impart on the matrix material including mechanical strength and electrical conductivity. However, chemically detecting and characterizing CNTs within these carbonaceous matrices can
be a significant measurement challenge. To that end, work has been performed to employ X-ray photoelectron spectroscopy (XPS) towards detecting multi-walled CNTs (MWCNTs) within polymeric matrices. MWCNT: epoxy composite samples of varying mass fraction were prepared and characterized by XPS in spectroscopy mode. Results revealed that the samples differentially charged and this behavior could be exploited to separate the less conductive, epoxy rich signal from the highly conductive, MWCNT-rich regions. Subsequent measurements involved XPS imaging which identified localized, conductive regions of interest (ROI) within the C (1s) spectra suggestive of higher CNT intensity. Hyperspectral XPS imaging was performed and processed using coding developed to extract spectra from these conductive ROIs and from the non-conductive ROIs. Results suggested that the conductive ROI was likely dominated by CNT aggregates and had only minor contributions from epoxy. Conversely, the charging ROI was most likely representative of a more dispersed, CNT composite that was epoxy rich. Raman imaging and SEM were employed as orthogonal measurements to confirm the XPS derived results. This research ultimately demonstrates a novel approach towards detection of CNTs in carbonaceous matrices and as a means for assessing the dispersion quality of polymeric composites.

COLL 225

Zwitterionic amphiphile based magnetofluorescent nanoparticles

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Magnetofluorescent nanoparticles (MFNPs) providing a single nanoscale platform with multimodal properties are gaining momentum in biomedical applications. They can enable simultaneous fluorescence labeling/imaging and magnetic field assisted separation, sorting, or heating. Conventionally, the surfaces of MFNPs are decorated with polyethylene glycol (PEG) to achieve their bioavailability and biocompatibility to cells/tissues. However, recent studies have indicated that zwitterions with better biocompatibility and more excellent non-fouling properties are alternatives to polyethylene glycol (PEG). In this work, a new amphiphilic polymer with zwitterionic carboxybetaine (CB) and sulfobetaine (SB) groups was synthesized and used for the fabrication of MFNPs. The MFNPs were prepared by integrating MnFe2O4 magnetic nanoparticles (MNPs), CuInS2/ZnS quantum dots (QDs), and zwitterionic amphiphilic polymer (ZW-polymer) in a tetrahydrofuran (THF)/water solvent system. Through sonication and quick solvent displacement, both MNPs and QDs are co-encapsulated within the hydrophobic core of ZW-polymer micelles. The fabricated MFNPs with around 100 nm average hydrodynamic diameters were found to be stable in PBS-5%FBS (pH4-11) solutions, 1M NaCl solution, and undiluted human serum over at least 72 hrs at 37 °C. The MFNPs were also found to be stable in water at 4 °C for over months. The stability of the MFNPs offers a great deal of flexibility for their applications in biomedical experiments. The optical properties and magnetic relaxivity of the MFNPs have been characterized. The cell viability study indicates the biocompatibility of MFNPs.
biotin-avidin bioassay using the MFNPs was performed and the assay data proved the bioconjugation capability of the MFNPs.

**COLL 226**

**Size-exclusive protein adsorption on plasmonic gold nanoparticles measured via optical dark-field spectroscopy**

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Many biological molecules, especially proteins, are able to connect among each other to oligomers or polymers. These associations are often the reactive or biologically relevant form of the protein. For example, polymers of actin and other proteins build up the cell skeleton. Some oligomers are thought to be a storage form of the protein that can be released if necessary, for example the protein Vipp1. Vipp1 is a protein highly abundant in chloroplasts and known to be relevant for the biosynthesis of thylakoid membranes. The protein can oligomerize to rings with sizes up to 2.2 MDa and recent studies show that it adsorbs preferentially to negatively charged lipids.[¹] To study whether this protein adsorption to membranes is takes place in oligomeric or imonomeric form, it is advantageous if the sensor-size approaches the molecular size of the protein. Herein we present the characterization of Vipp1-membrane interactions by single nanoparticle dark-field spectroscopy of lipid-coated gold-nanorods (Au-NRs). We measure the shift of the plasmon resonance wavelength (Δλ_{res}) induced by the adsorption of proteins. This shift is dependent amongst other factors on the size of the protein. By theoretically estimating Δλ_{res} for a Vipp1-ring adsorption and comparing it to Δλ_{res} measured over time during adsorption of the protein on our nanosensors, we can estimate that the predominantly adsorbed species on our sensors is not the oligomeric ring-form of Vipp1. The thermodynamic dissociation constant K_D = (0.38 ± 0.22) µM obtained in these experiments corresponds therefore to this species.

**COLL 227**

**Seed-mediated self-assembly to form core-shell and Janus nanostructure using nanoparticles-loaded thermo-cleavable polymer**

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We report the facile approach to control spatial distribution and self-assembly of nanoparticles for core-shell and Janus nanostructure (JNS) formation in amphiphilic diblock copolymer. We demonstrated that the gold/iron oxide Janus (Au/IONP JNS)
nanostructure formation could be achieved by seed mediated self-assembly mechanism of nanoparticle-loaded thermo-cleavable micelles (NP-TCM). Our thermo-cleavable polymer contains Diels-Alder cycloadducts in the hydrophobic backbone, which could be cleaved at high temperature resulting in the shortening and aggregation of the hydrophobic chains. This process leads to a structural transformation to maintain their thermodynamic stability. To trigger the self-assembly of nanoparticle-loaded micelle, free TCM seed and high temperature were introduced into the system to cause thermodynamic instability. After the hydrophobic backbones are disrupted, NP-TCM start fusing with the free TCM seed from an opposite direction resulting in structural reorganization and self-assembly to form core-shell or JNS. The structural transformation from cluster NP-TCM to the core-shell structure was clearly observed under transmission electron microscope (TEM) and scanning transmission electron microscope (STEM). Using this seed-mediated self-assembly, the asymmetrical Au/IONP JNS were developed and elucidated by using TEM, STEM, and x-ray energy dispersive spectroscopy (XEDS). The controllable seed mediated self-assembly process and subsequently formed core-shell and JNS will provide potential biological applications in drug delivery and imaging.

COLL 228

Synthesis and characterization of highly stable ligand protected quantum sized silver nanoclusters

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Recently, silver nanoclusters (AgNCs) became one of the extensively studied nanomaterials, owing to the low cost, abundance of the materials and interesting optical properties compared to gold nanoclusters (AuNCs). However, the low stability and the weak luminescence of the AgNCs has been a major challenge until now. In this poster, we present the synthesis and characterization of highly stable and water soluble AgNCs protected with glutathione (GS) and 3-mercapto-1-propylsulfate (MPS) ligands. The synthesis was carried out at 0°C by reducing silver nitrate with sodium borohydride in the presence of thiol ligands. Thus prepared cluster mixtures were further purified by poly-acrylamide gel electrophoresis (PAGE), which isolated two major clusters. Interestingly, one of the isolated clusters from the glutathione protected AgNCs showed a bright orange colored luminescence with a high quantum yield (~5 %). For further characterization of the isolated clusters, electrospray ionization mass spectrometry (ESI-MS), UV-vis spectrometry and fluorescence spectroscopy were carried out. These clusters were water soluble and found to be highly stable at room temperature for more than a year. The presence of sulfonate (MPS) and carboxylate (GS) terminal groups at the end of each ligands enabled facile modification on the anionic clusters by ion-pairing with functional cations. For example, the isolated AgNCs were ion paired with bulky tetraoctylammonium cations via phase-transferring reaction, for further studies on the electrochemical properties and the altered optical properties.
Thermal decomposition based synthesis of AgInS$_2$/ZnS quantum dots and their cellular imaging applications

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Quantum dots (QDs) have been very attractive in biosensing/imaging due to their unique optical properties (e.g., photostability, brightness). Unfortunately, the potential high toxicity of commonly used cadmium-based QDs for in vitro or in vivo applications has been a concern. Recently, cadmium-free I-III-VI QDs (such as AgInS$_2$ and CuInS$_2$ NCs) have been paid particular attention due to their low toxicity and environmental benignness. However, significant efforts are still needed in developing scalable synthetic approaches to produce sustainable high quality I-III-VI QDs for biomedical research. In this work, a one-pot thermal decomposition method to synthesize high-quality AgInS$_2$ and AgInS$_2$/ZnS QDs was developed. The quantum yields of the produced AgInS$_2$ QDs (yellow emission) and AgInS$_2$/ZnS QDs (green emission) are around 14% and 66%, respectively. The product yield per synthetic reaction is up to 60%. To further demonstrate their cellular imaging applications, AgInS$_2$/ZnS QDs were encapsulated within poly(lactide-co-glycolide)-block-poly(ethylene glycol) (PLGA-b-PEG) micelles through self-assembly, and the glioma-specific peptide chlorotoxin (CTX) was covalently coupled to AgInS$_2$/ZnS micelles. The further cell-micelle interaction study indicated that the CTX conjugated AgInS$_2$/ZnS micelles were specifically internalized into brain tumor cells U87 but not into non-glioma cells.

CO and CH$_4$ oxidation of unsupported and supported CuCeO$_2$ prepared in water-in-oil microemulsion

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Unsupported nano-ceria, CeO$_2$, catalyst mixed with different percentages of CuO (5%, 10%, 15%, 30%, 40% and 50% by weight) was prepared by microemulsion method stabilized by surfactants mixture (DDAB and Brij®35). The catalytic activities of the unsupported catalysts were tested towards total oxidation of CO and nano-ceria mixed with 50 wt% CuO was found to exhibit the highest activity and the lowest oxidation temperature (< 200 °C). This catalyst was also supported over TiO$_2$, SiO$_2$ and Al$_2$O$_3$. The supports were also synthesized by microemulsion method. The catalysts were characterized by XPS, SEM, and nitrogen sorptiometry. The surface area study of the supports indicates that SiO$_2$ possess a high BET surface area of 1014.5 m$^2$/g. The results show that the unsupported CeO$_2$ catalyze the CO oxidation and obtained full
conversion to CO$_2$ at 300°C while adding CuO to CeO$_2$ (up to 50%) decreases the total oxidation temperature of CO to 200°C. The supported catalysts were also tested towards methane combustion, and according to the results, silica supported CuCeO$_2$ shows the best catalytic performance among the three supported catalysts.

Isotherms of microemulsion-synthesized metal oxides

**COLL 231**

**Tumor targeted poly(ethylene glycol)-poly(D,L-lactic acid)-based copolymeric micelles as a potential chemotherapeutic drug delivery system: Synthesis, physico-chemical, and in vitro characterization**

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The aim of present study is to develop a chemotherapeutic drug, curcumin (CUR) loaded, biodegradable and self-assembled poly(ethylene glycol)–poly-D,L-lactide (MPEG–PLA) copolymer-based polymeric micelles, the surface of which would be conjugated to a tumor homing protein, transferrin (Tf) for active targeting of nanocarrier to cancer. CUR is highly efficient in killing cancer cells by inhibiting cancer cell proliferation, and apoptosis, however, poor water solubility and limited bioavailability
restricts its clinical application. In our study, curcumin was incorporated into the hydrophobic core of the micelles. Maleimide functionalized MPEG-PLA was self-assembled with PEG-PLA at mol ratio 2% of the PEG-PLA during the micelles preparation for conjugation of thiol-derivatized transferrin on the surface. The preparation process was optimized with a central composite design (CCD). The images of transmission electron microscopy showed that the optimized CUR-MPEG-PLA were spherical and well dispersed. The average size of the micelles was 110 nm as measured by dynamic light scattering. The encapsulation efficiency for CUR was 92.41% with loading capacity of 11.15%. Compared to the conventional CUR-propylene glycol solution, the in vitro release of CUR from CUR-MPEG-PLA exhibited sustained-release (Fig 1). The results indicated that Tf-conjugated micelles were taken up by the cancer cells more efficiently compared to plain micelles (PL). The in vitro cell viability study demonstrated that the Tf-anchored micelles delivered drugs more efficiently to the cancer cells compared to PL, resulting in enhanced therapeutic activity. Therefore, newly developed cancer targeted micellar system could be utilized as a potential carrier for the delivery of curcumin in cancer improving its bioavailability significantly compared to conventional therapy.

**Figure 1**: Profiles of the cumulative release percentage of curcumin from polymeric micelles (■) and the propylene glycol solution (●) at pre-set time point in physiological saline containing 5% SDS at 37 °C. Each point represents average ± SD (n = 3).

**COLL 232**

*Stimulus-responsive water-soluble graphene nanodevices for tunable biomarker detection*
It is still in high demand to develop tunable/controllable tools for in situ detection of biomarkers for the diagnosis and prognosis of diseases and monitoring their response to therapy. The “Always-On” property of current sensing systems lead to off-target effects and high background signal. An efficient way to overcome these shortcomings is to engineer a nanodevice that could act as an activatable biosensor and turn "on/off" in response to external stimuli. Here, we report smart graphene-based nanodevices which can controlled for the detection of various biomolecules. Our system is composed of nano-graphene oxide nGO, serves as a fluorescence quencher and template for the probe DNA strands, and a thermoreponsive PEGMA (poly(ethylene glycol) methyl ether methacrylate) polymer serves as an activatable protecting layer over DNA molecules. The concept is based on the fact that PEGMA polymers are hydrophobic above their lower critical solution temperature (LCST) and lay tightly on the hydrophobic surface of nGO. This creates the closed configuration (OFF state) of the nanodevice and entraps the surface adsorbed probe DNA strands. However, once the temperature decreases below the LCST, the polymer undergoes conformational change and becomes hydrophilic. This opens up the surface of the nGO (open configuration, ON state) and frees the encapsulated payload on the surface. Fluorescence studies showed two distinctive release kinetics with temperatures above and below the LCST value. The nGO-PEGMA showed a strong retention strength when the temperature is above the LCST value and almost no retention when below. We have controlled the activity of the nanodevice for the detection of four different biomolecule types: a sequence-specific DNA, miR-10b, thrombin, and adenosine. The activity of our functional system can be decreased by ~80% with a thermo-switch at 39 °C. This work provides a simple yet powerful approach with great potential in precise control over the activity of the functional material with minimum off-target effect and background signals.
Controlling the biomolecule detection capacity of activatable graphene nanodevices with a thermoswitch.

**COLL 233**

**Tuning the detection capacity and specificity of polymer protected graphene nanoassemblies using endonucleases**

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Nanoscale materials have attracted researchers for their outstanding features and possible applications in biological and biomedical sciences. Graphene oxide (GO) is a one-atom-thick two-dimensional carbon nanomaterial with such outstanding properties. Recently, it has gained remarkable attention as a platform for the detection of small RNA biomarkers, known as microRNAs (miRNAs). These miRNAs, or oncomiRs (oncogene miRNA), are about 22 base pairs in length, have been found to be dysregulated in many types of cancer, capable of intricate control of the cellular workings and a reliable biomarker for the disease. In breast cancer specifically, miR-10b is an up-regulated miRNA which is not only a marker for the disease, but also a marker for metastatic breast cancer. Recently we have shown precisely how enzymatic amplification, a technique newly utilized to lower the detection limit of target miRNAs, vastly increases the signal strength over normal hybridization detection. Through examination of the mechanism of action of DNase I, we were able to both better understand how to optimize the detection of this oncomiR as well as visualize the shortcomings of the technique. Here we have demonstrated that by using selectively placed mismatches in our fluorescent probes and by functionalizing nGO with poly (ethylene glycol) monomethyl ether methacrylate (PEGMA), we are able to dramatically increase selectivity of our target over other similar sequences and completely remove
background activity of the enzyme on our nanoassembly. These improvements allow reliable and specific signal generation system where we can quantify the concentration of oncomiR present.

The thermoresponsive polymer (PEGMA) coating protects the probe strands from nonspecific cleavage by DNase I and enables tuning the detection capacity of the nanoassembly.

**COLL 234**

**Two-color detection of circulating miRNAs from liquid biopsies for prostate cancer screening using graphene nanoassemblies**

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Circulating miRNAs are highly stable diagnostic and therapeutic tumor biomarkers, which can reflect the status of the disease. *miR*-141 is an oncomiR, which is overexpressed in advanced prostate cancer patients, whereas its expression is at the normal levels in the early stages of the disease. On the other hand, *miR*-21 is significantly elevated in the early-stage, but not in the advanced prostate cancer. Here, we have demonstrated simultaneous detection of *miR*-21 and *miR*-141 from human liquid biopsies including blood, urine and saliva using graphene nanodevices. Our system enables us to specifically and reliably detect each oncomiR at two fluorescence emission channels from a large population of RNAs extracted from body fluids. We have also demonstrated that the sensitivity of our diagnostic nanodevices can be tuned by incorporating a highly specific enzymatic step. The approach in this study combines two emerging fields of nano-graphene in biomedicine and the role of circulating miRNAs in cancer. The reported graphene nanodevice is simple to assemble and operate. The prostate cancer screening approach using liquid biopsies is non- or minimally invasive.
and can be combined with the current diagnostic methods to minimize low selectivity and sensitivity. Our approach also enables us to identify the aggressiveness of the disease. Therefore, the strategy reported here has the potential to address the current challenges in diagnosis, prognosis and staging of prostate cancer with a non- or minimally invasive approach.

Simultaneous detection of miR-141 and miR-21 using graphene DNA nanoassemblies.

**COLL 235**

**Highly sensitive enzyme-free detection of multiple miRNAs using gold nanoparticles and hybridization chain reaction**

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MicroRNAs (miRNAs) are small noncoding RNA molecules (~22 nucleotides) that regulate gene expression at the post-transcriptional level. Expression of certain miRNAs has been found to be deregulated in the tumor tissue and liquid biopsies of the cancer patients. Although miRNAs are superb tumor biomarkers, their use in clinical setting has not been demonstrated in detail due to the current limitations of miRNA detection methods. The current miRNA detection methodologies are expensive, laborious and time consuming. Here we report highly sensitive and selective miRNA detection methodology using gold nanoparticles and hybridization chain reaction. Our method is enzyme-free and enables detection of multiple miRNAs simultaneously. In the
experimental design, two hairpin auxiliary probes (H1 and H2), an initiator (it opens hairpin probe H1), and a thiol captured 36-mers (probe DNA) conjugated gold nanoparticles are used for detection of a miRNA. First, thiol modified 36-mers capture-DNA probes are immobilized on gold nanoparticles and then the target miRNA partially hybridizes with the capture-DNA probes. Later the initiator binds to the miRNA and capture-probe assembly and forms a nucleic acid nanoparticle construct with sticky ends. A sticky end triggers to open a hairpin H1, which exposes a new single-stranded region that initiates to open H2 and the identical HCR process occur. Our preliminary results suggest that using this enzyme free and isothermal signal amplification method is able to detect low copies of miRNAs. Our novel approach is rapid, cost-effective, easy to perform, extremely sensitive and selective.

Highly sensitive fluorescence detection of miRNAs using gold nanoparticles and hybridization chain reaction.

COLL 236

Self-assembled glycinin colloidal nanoparticles-stabilized gel-like oil-in-water Pickering emulsions as a potential sustained-release and intestine-targeted delivery system for coenzyme Q10

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In recent years, the development of food-grade biopolymer nanoparticles-stabilized Pickering emulsions as promising delivery systems for bioactive components has attracted growing interests. This study reported that glycinin, the major globulin in soy proteins, mainly presents in the self-assembled nanoparticle form (with a z-average diameter of 89 nm) after heating pretreatment at 100 °C. These nanoparticles-stabilized emulsions at pH 7.0 exhibited a great potential to act as intestine-targeted and sustained-release delivery systems for coenzyme Q10. The emulsions were fabricated
by microfluidization at a specific protein concentration of 4.0% (w/v) and varying oil fractions (φ) of 0.2-0.5. The results indicated that increasing φ can result in a gradual structuring of prepared oil-in-water emulsions. The formation of gel-like network was mainly attributed to droplet flocculation. The release behavior of coenzyme Q10 during in vitro simulated intestinal fluid in these emulsions could be controlled via changing φ value. The gel-like emulsion at φ = 0.5 exhibited much lower release of coenzyme Q10, but higher stability towards degradation during the digestion process, than that at φ = 0.2. The findings are of great importance for designing food-grade Pickering emulsions as promising oral delivery systems for lipophilic bioactive compounds.

COLL 237

**Emulsifying and interfacial properties of soy globulins: Role of conglycinin in the formation of oil-in-water microemulsions**

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The emulsifying and interfacial properties of conglycinin/glycinin blends with varying glycinin content in aqueous solutions were characterized. The results indicated that the emulsifying ability and emulsion stability (against flocculation, coalescence and even creaming) of blends considerably varied with glycinin content. In general, conglycinin exhibited much better emulsifying capacity than glycinin. There were certain interactions between conglycinin and glycinin in aqueous solutions. Increasing glycinin content basically inhibited the formation of the fresh emulsions with more flocculated oil droplets, which was confirmed via microstructure (confocal laser scanning microscope) and flocculation index (FI) data. Interfacial protein content (AP %) and composition (SDS-PAGE) suggested that 75 % conglycinin (total metastable concentration c = 0.5 %, m/v) was sufficient for the effective stabilization of corresponding blends-stabilized emulsions. The differences in emulsifying properties of these blends with different glycinin content could be to a certain extent attributed to the variations in their interfacial properties, including interfacial protein concentration (Γ), ζ-potential and conformational flexibility, as well as diffusion, adsorption, unfolding, permeation and structural rearrangement at the interface (Optical Contact Angle). These results are of great importance for extending current knowledge about the properties and stability of soy globulins-stabilized oil-in-water emulsions that exhibit excellent potential to be applied in drug or food formulations, e.g., as micro- or nano-scale oral delivery systems for environment-sensitive ingredients (e.g., protein drugs or vaccines).
Pea protein isolate as a natural nanocarrier for enhanced dispersibility and stability of curcumin

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This work reported pea protein isolate (PPI), a type of amphiphilic biopolymers, mainly presented in the nanoparticle form with the hydrodynamic diameter of 70-90 nm in solutions (Dynamic Light Scattering and Atomic Force Microscopy). Curcumin as a model drug was encapsulated successfully into pea protein nanoparticles with a simple, low-energy and toxic solvent-free method. PPI nanoparticles did not suffer noticeable changes in particle size and morphology upon complexation with curcumin, while the surface hydrophobicity markedly decreased. Fluorescent data exhibited that quenching process between PPI and curcumin was primarily attributed to static quenching by the formation of PPI-curcumin nanocomplexes. Fourier transform infrared spectroscopy and Circular Dichroism patterns further confirmed successful complexation and its influence on the secondary structure of pea proteins. After complexation, the solubility and thermal stability of curcumin were both considerably enhanced. The degradation of
Curcumin under complexation conditions was negligible (confirmed by nuclear magnetic resonance spectroscopy). The results suggest PPI can be utilized as a promising natural nanocarrier for nanoencapsulation and oral delivery of lipophilic drugs or nutraceuticals in food and pharmaceutical formulations.
Synthesize and characterization of bis-cationic surfactant and self-assembly into worm-like viscoelastic fluids

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In this paper, a bis-cationic surfactant C21H41CONHC3H6N+(CH3)2-(CH2)6- N+(CH3)2NHCOC21H412Br-, referred to as C25-6-C25, has been synthesized mainly for thickening purpose. The characterization of C25-6-C25 were performed by 1H NMR spectra recorded with the sample dissolved in CDCl3. Additional support was given by infrared spectra in the spectral range of 4000-400 cm⁻¹ with a resolution of 2 cm⁻¹. Critical micellar concentration of the surfactant in aqueous solution determined by tensiometry and conductometry were observed to be 0.45mmol/L and 0.60mmol/L, respectively. The rheological behavior and morphology investigation were performed to understand the solution properties of C25-6-C25 in the presence of potassium chloride (KCl) with four factors changed including the surfactant concentration, KCl concentration, temperature and pH of the solution. The results show that the viscosity increases with the increase of C25-6-C25 and KCl, but decreases when increases of the temperature. The viscosity of this gemini surfactant solution can meet the demand...
of hydraulic fracturing under 125°C. The fluid maintains the highest viscosity in neutral solution. Scanning electron microscope (SEM) observation confirmed the formation of three dimensional networks, in which branched worms are made up of elongated surfactant micelles, in good agreement with the experiments results. We conclude that C25-6-C25 fluids show high viscosity, better stability at high temperature due to the long hydrophobic C25 tail.

$^1$H NMR of the bis-cationic surfactant
SEM image of a 12mmol/L C25-6-C25 solution in the presence of KCl

**COLL 240**

**Stepwise functionalization method for nanostructure-based Mg₉Zn₁₋ₓO biosensor with increased sensitivity and selectivity**

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Immobilization and detection of biomolecules on various functionalized material surface is important for development of highly sensitive and selective biosensors. Among all the materials, nanostructured ZnO (nano-ZnO) is a particularly promising one for biosensor technique after appropriate functionalization due to its multifunctional properties and tunable energy bandgap through proper doping, high surface area, fast and reversible surface wettability, controllable surface morphology and biocompatibility. Nano-ZnO has already been employed for the detection of intracellular pH, proteins, DNA/oligonucleotides and antibodies. However, the application of nano-ZnO is considerably limited as a result of instability of ZnO to acids and bases. For example: The morphology of ZnO nanorod will be damaged when reacting with alkynated folic acid. Nano- MgₓZn₁₋ₓO has similar properties and binding properties to those of nano-ZnO. The material remains intact over a wider pH range (pH 3-9.5), making it an attractive alternative for nanostructured ZnO.

We report the functionalization of nano-MgₓZn₁₋ₓO through well-controlled stepwise method. It involves first the attachment to the surface of heterobifunctional linkers through one anchoring group, leaving an end-group available for further immobilization of proteins or small molecules that interact with proteins or cells (folic acid-breast cancer cell interaction). The copper-free click reaction was explored here. The use of MgₓZn₁₋ₓO broadens the functional groups suitable for the binding. We also show the increased coverage of bifunctional molecule on MgₓZn₁₋ₓO surface by eliminating competing reaction of solvents. The study of other anchor groups and linker units onto MgₓZn₁₋ₓO will be also discussed.
Hydrophobicity of treated graphene oxide surfaces: Experimental and molecular dynamics simulation studies

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Carbon-based nanomaterials such as graphene are excellent candidates for superhydrophobic surfaces because of their intrinsically high surface area, nonpolar carbon surface, low density and high surface roughness. Recent studies have shown that the contact angle of water on graphene is in the range of 90 to 95°. In the present work, appropriate molecular dynamics simulation parameters for graphene surfaces were determined in order to get the correct water contact angle. Computational modeling methodology was developed to characterize the nanoscale wettability of functionalized graphene surfaces. Treated graphene surfaces with both fluoro and non-fluoro alkyl silane coupling agents were prepared. In the case of fluorinated coupling agents, a new energy parameter for fluorine atoms was found using optimization of hydration free energies. The water contact angles with different droplet sizes were characterized and extrapolated to the micro-size water contact angle. The contact angle showed an enhancement with increasing the density of coupling agents. Experimentally, treatment of graphene oxide with both fluoro and non-fluoro silane coupling agents was performed using p-toluene sulfonic acid catalyst at 50 °C in a mechanical shaker. After treatment of graphene oxide with silane coupling agents, significant increase in contact angle was observed and theoretical and experimental results have been compared.
Porous polymeric membrane formed by charge and amphiphilicity dually driven self-assembly

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A biomimetic membrane is a key component of biosensors and biofuel cells. It is crucial for a bioactive molecule to sustain its bioactivity as well as to reach a high concentration in a membrane. An ordered arrangement of biomolecules in a membrane and exposure of their electroactive centers are also desirable for a high sensitivity. This paper demonstrates a facile method to form a porous polymeric membrane, immobilizing a biocatalyst. A polyelectrolyte based amphiphilic diblock copolymer, i.e., polystyrene-block-polyacrylic acid (PS-b-PAA), self-assembles with hemoglobin (Hb) dually driven by charge and amphiphilicity during solution casting and evaporation. The results indicate that the hydrophobic block enriched on the membrane surface. The hydrophilic block points toward the internal membrane as well as directed the Hb arrangement at the interface of the polymer layer and electrode. The obtained electrode shows a remarkably enhanced direct electron transfer. The membrane has been tested to catalyze the reduction of hydrogen peroxide, and exhibits an excellent reproducibility and stability. This method with a charge and amphiphilicity dually driven (CADD) self-assembly creates a way to construct a third generation electrochemical biosensor.

Multifunctional theranostic silica-gold core-shell nanoparticles for breast cancer applications

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Breast cancer (BrCa) is the second leading cause of cancer death in women and this year about 40,000 women are predicted to die from BrCa. About 10-20% of BrCa are found to be triple negative, an even more severe type of BrCa that has lower survival rates. Triple negative BrCa (TNBC) does not express the genes for hormone epidermal growth factor receptor 2 (HER-2), estrogen receptors (ER), and progesterone receptors (PR) which means hormone therapy and drugs that target these receptors are ineffective means of treatment. Recently the use of nanoparticles has become popular and this research focuses on the synthesis and characterization of multifunctional theranostic silica-gold, core-shell nanoparticles (SGCSNs) which will be used for imaging and photothermal therapy of TNBC. The nanoparticles were synthesized by first making a silica core, reducing the amount of gold used during synthesis, and then seeding the core with gold nanoparticles to form a gold shell. A bifunctional PEG was attached to the surface of the synthesized nanoparticles; one end has a thiol ligand
attached which bonds to the gold shell of the nanoparticles by a gold-sulfur bond and the other end has folic acid attached which binds to the folate receptor which is seen to be over expressed in many TNBCs. A gold shell was chosen for the synthesis of the nanoparticles because gold serves as a good agent for CT scanning because of its high Z value which makes the nanoparticles ideal for imaging. Also because of surface plasmon resonance, gold nanoparticles can be used to destroy cells through photothermal therapy. The theranostic SGCSNs were synthesized characterized and a bifunctional PEG was attached for applications in imaging and photothermal therapy of TNBC in vitro, using MDA-MB-231 cells. If successful SGCSNs could be useful in both imaging and photothermal therapy and could greatly improve the quality of life of TNBC patients.

 COLL 244

Mg@porous SiO₂ particles: Preparation, controlled hydrogen release, and hydroxyl radicals scavenging activities

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Hydroxyl radical (·OH) is the strongest oxidant specie, and could cause many diseases such as cancer, Alzheimer’s disease etc.. Hydrogen (H₂) molecule, which is usually introduced in hydrogen gas or saturated solution, is an ideal antioxidant in preventive and therapeutic applications to selectively and effectively reduce ·OH. However, inhalation of hydrogen gas and H₂-rich water is unsuitable as continuous hydrogen consumption for preventive use. In this work, we have demonstrated the controllable and continuous release of H₂ by using Mg@porous SiO₂ microparticles to scavenge ·OH in the biological medium, preventing oxidative damage of PC12 cells. The Mg@porous SiO₂ particles are synthesized by a modified Stöber method using acetone as the solvent. Hydrogen molecules are generated and continuously released from the Mg@porous SiO₂ particles through the Mg-H₂O reaction\(^1,^2\) under the action of the pit corrosion and the buffering effect of simulated body fluids (SBF) or blood plasma. The release rate of H₂ can be controlled simply by adjusting the diffusion barrier of silica shells with varied thickness, and hence the concentration of ·OH can be controlled at a low level and the viability of PC12 cells maintain up to 6 h in a harsh environment with continuous injection of ·OH. Furthermore, the silica shell can be easily modified with other silane coupling agents or responsive polymers, suggesting that the as-proposed Mg@porous SiO₂ particles also can act as a smart H₂ reservoir for H₂ release under different stimuli\(^3\) thus hold promises for their practical biomedical applications.

References:
Synthesis and optimization of colloidal gold nanoparticles for cancer therapy

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With the rising appearance of cancer in modern society, many forms of therapy have been developed to impede and eliminate the impact of cancer in human and animal cells. The use of nanoparticles for anti-cancer drug delivery is one strongly desirable method to accomplish such a task. Unlike previous treatments such as radiation and chemotherapy, loaded liposomes can be specifically targeted to attack cancer cells in vivo. The ability to target this shipment of anticancer drugs directly to cancer cells, avoiding all other healthy cells, is greatly beneficial to overall normal cell health and survival rate. In addition to anti-cancer medication, certain metallic nanoparticles have also been experimented with for imaging purposes. In this project we have been working to optimize the construction of colloidal gold nanoparticles (AuNPs) for cancer
treatment and diagnosis. AuNPs have shown great potential as both a photothermal therapy (PTT) and photodynamic therapy (PDT) approach towards cancer detection and treatment. Combined with fluorescent, therapeutic agents such as Methylene Blue, AuNPs can enhance the contrast and fluorescence provided by multimodal imaging to clearly differentiate cancer from normal cells. In addition to detection, AuNPs can also contribute to the treatment of cancer cells as they can absorb and magnify light waves to deteriorate the cancer. The challenge with using stock factory AuNPs lies in the occasional inconsistency between actual size of the particles and the size reported. There is also little to no flexibility in changing the size and compositions of AuNPs once they have been already made. For these reasons, we are experimenting with the synthesis of our own AuNPs in lab for use in liposome loading. The goal is to optimize and establish a simple and effective SOP that can be used in an academic lab setting for the synthesis of these particles. It is very important that the size desired can be achieved consistently and that it remains constant over time while being stored. Optimization of these particles will focus on multiple factors including molar ratios of chloroauric acid (HAuCl4) and sodium citrate (Na3C6H5O7), volume of water (H2O), concentration of sodium hydroxide (NaOH), reaction temperature, and reaction time. By optimizing the size and uniformity of AuNPs, we can hopefully provide a consistent supply of particles for use in liposome encapsulation in future in vitro trials.

COLL 246

Charge transport by tunneling through SAMs

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This talk will outline studies of the mechanism of charge transport by tunneling across SAMs in junctions of the form Metal (Au or Ag)/SAM//Ga2O3/EGaIn.

COLL 247

Longing for Langmuir

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The Langmuir adsorption isotherm is the first equation learned by all good surface chemists. Its beautiful simplicity directly reflects the simplicity of the system: a single type of molecule is in dynamic equilibrium with a single surface site, up to monolayer coverage. This simple picture can approximate many real systems; yet many real systems are far too heterogeneous for the Langmuir isotherm to apply, even though we all long for Langmuirian simplicity. In this talk I will discuss how many of the details we are learning about biomolecular adsorption on gold nanoparticle surfaces are at cross-purposes with every one of the assumptions of the Langmuir adsorption isotherm: there
can be non-equivalent sites on the surface; there is multilayer coverage; and surface site material can be transferred to the nominal adsorbate.

**COLL 248**

**Adsorption at the bio/nano interface: DNA, liposomes, and inorganic nanoparticles**

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In this talk, our recent work on the adsorption of biopolymers (mainly DNA and liposomes) by various inorganic nanoparticle surfaces will be presented. Our study supports that DNA is adsorbed by metal oxides via the phosphate backbone, by graphene oxide via pi-pi stacking and by noble metals via base coordination. These fundamental adsorption studies enabled a number of new applications in biosensor development and DNA delivery. The second half of the talk will be devoted to the adsorption of zwitterionic phosphatidylcholine liposomes, where interesting surface forces have been revealed for the binding interaction. For example, metal oxides can adsorb the liposome via phosphate interaction, thus forming quite stable hybrid material, while graphene adsorption is strongly dependent on the oxidation level. Gold nanoparticles induce transient liposome leakage due to local phase transition of the lipid bilayer, possibly due to very strong van der Waals force. These studies highlights the importance of various intermolecular forces and will enhanced our fundamental understanding of the bio/nano interface.

**COLL 249**

**Biological and environmental media control oxide nanoparticle surface composition: The roles of biological components (proteins, peptides and amino acids), inorganic oxyanions, and humic acid**

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Nanoparticle surfaces have high free energy and therefore thermodynamic driving forces will work toward minimizing the surface energy. In order to achieve a lower energy state, nanoparticles undergo different physical and chemical transformations including reconstruction, aggregation, dissolution and ligand adsorption. In environmental or biological systems, the surrounding milieu will drive these interactions. Therefore it is important to consider nanoparticles as dynamic entities that undergo rapid transformations that depend on the solution pH, ionic strength and composition. A focus of this talk will be to highlight a few examples of in situ characterization of oxide nanoparticle surfaces in different environmental and biological media so as to show the importance of the milieu on surface composition. The surface composition is shown to be vastly different in different media with adsorption of biological components (proteins,
Wetting of solids by liquids

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During the last 4 decades our research group has studied the wetting of solids by liquids. These studies began with the use of contact angle as an analytical technique to study organic polymer surface chemistry. We had the goal of controlling properties such as coefficient of friction and ice adhesion by first correlating surface chemistry with surface properties. In retrospect we were naive - about many things. We measured thousands of contact angles during this work, but didn't think about wetting at a fundamental level and just focused on using the data to follow the chemistry. Later we became interested in polymer adsorption and studied the adsorption of many polymers to many surfaces. We used contact angle again to try to gain insight into thin film structure and to determine adsorption and desorption kinetics - but again we did not think about wetting at a fundamental level.

So contact angle analysis had a constant presence in our work as an analytical tool, but we did not think about wetting from a physics perspective until "superhydrophobicity" was born in the late 1990s while we were studying covalently attached monolayers on silicon wafers (to remove topography as an issue in contact angle analysis. We published 6 papers in 1999 and 2000 (five in Langmuir) to address these issues, and determine the length scales of topography that were important to both contact angle hysteresis and superhydrophobicity. This field became very popular in the first decade of the 2000s and we "re-entered" the field and published several papers in 2006 and 2007 in attempts to change the way people looked at wetting including "Contact Angle Hysteresis Explained," "A Perfectly Hydrophobic Surface: $\theta_A/\theta_R = 180^\circ/180^\circ$" and "How Wenzel and Cassie Were Wrong."
Synthetic compounds/materials-biological interface: A doorway to new opportunities for sensing, antimicrobial activity, and therapeutics

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Our presentation will introduce a class of materials and compounds based on charged phenylene ethynylene polymers (CPE) and oligomers (OPE) that we have used as fluorescence-based biosensors and antimicrobials over the past several years. The focus of the presentation will be on recent findings and new applications we have developed. The first example is our finding that certain OPE and CPE can induce or enhance bacillus spore germination in a dark process. This provides a new mode of antibacterial activity in that the resulting vegetative can be killed by either dark or light-activated biocidal activity of the same OPE or CPE. We will also show how the CPE and OPE can be formulated into wet or dry wipes that may provide a versatile and inexpensive decontamination or disinfection of a variety of surfaces. Another topic we will discuss is the selective binding of certain OPE with fibrils formed from aggregation of mis-folded proteins associated with Alzheimer’s disease and sensing and therapeutic possibilities that might be developed from these interactions. Finally we will discus recently developed fluorescence sensing that we have constructed via self assembly of OPE aggregates with amphiphilic biochemical subject to cleavage via enzyme activity.

Maintenance and differential regulation of stem cells using functionalized nanoparticle monolayer

Which surface is more hydrophobic?
We have generated monolayers of different nanoparticles on negatively charged polystyrene surfaces. These monolayers are robust under cell culture conditions, with no cellular uptake of nanoparticles observed after one week culturing. By choice of nanoparticle ligands, cell growth and behavior are selectively regulated. We will discuss the behavior of a variety of cell types on these surfaces, including recent studies of mesenchymal stem cells.

**COLL 253**

Retaining protein and fluorophore activity attached to graphene oxide

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Pyrene-based noncovalent binding motifs have become one of the pioneering strategies to interface 2-D atomic material graphene and graphene oxide (GO) with biology. We previously developed molecular tripods as a multivalent pyrene-based binding motif for interfacing proteins with graphene, which promise a robust strategy for fabricating graphene-based biosensors and bioelectronic devices. Here we demonstrate a general strategy to functionalize GO nanosheets noncovalently using tripod binding motifs. Tripods immobilize the serine protease enzyme chymotrypsin (ChT) onto GO and preserve its native structure and activity. In contrast, unmodified GO is one of the strongest known ChT inhibitors. Furthermore, GO quenches the photoemission of many fluorescent probes and its weak inherent photoemission is inconvenient for imaging via fluorescence microscopy. When interfaced to GO through a tripod, the fluorescent dye Alexa Fluor (AF) 488 retained its fluorescence, allowing the GO sheets to be imaged using a standard fluorescence microscope. As such, tripod binding groups represent a
useful strategy to functionalize GO with biomolecules and study its interactions with cells and living organisms.

Protein Attached to Molecular Tripods for Interfacing with Graphitic surfaces

COLL 254

Increasing the stability of semiconductor quantum dots in biological solutions through surface chemistry

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Luminescent quantum dots (QD) have been used extensively in recent years as an alternative to molecular organic fluorophores in bio-imaging applications. This is due to their unique photo-physical, including high photo-stability, broad absorption and narrow emission peaks, high emission quantum yield, and size dependent emission. To date, fluorescence microscopy measurements of QD-cell involved short incubation, of one hour of less, of cells to luminescent QD. These experiments are also typically conducted in minimal cell media to prevent QD aggregation. The use of QD in experiments, which require longer incubation of luminescent QD with cells or whole organisms requires significant improvement in ligand technology compared to the current state-of-the-art. The goal of this study is to develop an advanced ligand technology to significantly improve the stability of luminescent QD in biological solutions of increasing complexity, including in cell media. To this end, we have prepared a series of bi-thiolated ligands
that contain varying polyethylene glycol (PEG) moieties in their structure. We are in the process of capping InP/ZnS and CdSe/ZnS QD with these ligands. We anticipate that an optimal PEG length will maximize the QD chemical stability and minimize aggregation. A wide array of analytical measurement techniques including high resolution transmission electron microscopy (HR-TEM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), UV/VIS absorption, and fluorescence spectroscopy and microscopy are used to characterize the chemical stability and photophysical properties of the resulting QD in aqueous buffer solutions and cell media. We aim to develop a versatile synthetic approach for ligand synthesis that can accommodate a large variety of chemical environments.

COLL 255

Lasting alteration of compositional membrane asymmetry by LiCoO2 nanoplates

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Given the projected massive presence of redox-active nanomaterials in the next generation of consumer electronics and electric vehicle batteries, they are likely to eventually come in contact with cell membranes, with biological consequences that are currently not known. Here, we present nonlinear optical studies showing that lithium nickel manganese cobalt oxide nanoplates carrying a negative $\zeta$ potential have no discernable consequences for lipid alignment and composition in supported lipid bilayers formed from zwitterionic and negatively charged lipids. In contrast, lithiated and delithiated LiCoO2 nanoplates having neutral to positive $\zeta$ potentials alter the compositional asymmetry of the two membrane leaflets. The results indicate the bilayer asymmetry remains disturbed even after rinsing, suggesting alterations to the membrane are not restored following contact. The insight that some cobalt oxide nanoformulations cause lasting alterations to the compositional asymmetry in idealized model membranes may represent a first step towards assessing the biological consequences of their predicted widespread use.

COLL 256

Mimicking complex virus-cell interactions with rationally engineered nanoparticle surfaces

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Nanoparticle surfaces provide unique opportunities for manipulating cell-nanoparticle interactions. Both the ability to control physical surface properties (curvature, hydrophilicity) as well as the ability to present specific ligands in a multivalent fashion make it possible to manipulate nanoparticle – cell interactions. This presentation outlines the molecular engineering principles underlying lipid wrapped metal
nanoparticles that reconstitute the uptake and sequestration of the human immunodeficiency virus (HIV) in a glycoprotein independent fashion. Integration of the glycosphingolipid GM3 in a nanoparticle tethered membrane is sufficient to achieve a sequestration of the nanoparticles into non-lysosomal compartments located in close contact to the plasma membrane. T cells are observed to bind preferentially in the vicinity of the nanoparticle enriched compartments resulting in an enrichment of nanoparticles at the dendritic cell – T cell synapse.

**COLL 257**

**pH-Responsive framboidal vesicles prepared using polymerization-induced self-assembly via RAFT aqueous dispersion polymerization as virus mimics**

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A series of pH-responsive methacrylic triblock copolymer vesicles were prepared in water from precursor diblock copolymer vesicles via RAFT seeded emulsion polymerization. More precisely, a poly(glycerol monomethacrylate) macromolecular chain transfer agent (PGMA macro-CTA) was chain-extended with 2-hydroxypropyl methacrylate (HPMA) via RAFT aqueous dispersion polymerization to prepare a 100 g batch of PGMA-PHPMA diblock copolymer vesicles. In a series of subsequent experiments, portions of these PGMA-PHPMA precursor vesicles were chain-extended using varying amounts of 2-(diisopropylamino)ethyl methacrylate (DPA) via RAFT seeded emulsion polymerization to prepare a range of PGMA58-PHPMA300-PDPAz triblock copolymers, where z was systematically varied from 86 to 460. TEM, DLS and SAXS studies confirm that these framboidal vesicles (see Figure 1) remain intact at neutral pH, but undergo irreversible dissociation on addition of acid. At pH 3, protonation of the tertiary amine groups leads to vesicular dissociation to cationic spherical micelles. More recently, these triblock copolymer vesicles have been modified to mimic the dengue fever virus. Optimization of the steric stabilizer, the surface morphology, and the vesicle diameter have been investigated in order to improve cellular uptake. These nanoparticles were synthesized successfully in sterile conditions by RAFT aqueous polymerization. Sterility tests have shown that the designer nanoparticles are sterile, proving that RAFT polymerization can be achieved in sterile conditions. Moreover, MTT tests have shown that these framboidal vesicles are biocompatible. Initial results suggest that these novel nanoparticles can be used to efficiently target specific breast cancer cells.
**Figure 1.** Above: Synthetic route used to prepare framboidal PGMA$_{58}$-PHPMA$_{300}$-PDPA$_z$ triblock copolymer vesicles via RAFT aqueous dispersion polymerization at pH 7-8. Below: Representative TEM images obtained for the smooth PGMA$_{58}$-PHPMA$_{300}$ diblock copolymer precursor vesicles and framboidal PGMA$_{58}$-PHPMA$_{300}$-PDPA$_{86}$ triblock copolymer vesicles.

**Surface modification to control cell/surface interactions**

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Multifunctional hybrid materials composed of nanoscale building blocks (e.g. nanoparticles, liposomes, polymeric materials incorporating different dyes, drugs, nanoparticles and biomolecules, etc.) have vast applications in biology such as in targeted drug/gene delivery and biosensing. Interaction of these materials with cells mostly depends on the size, shape, aspect ratio, elasticity and surface chemistry of the interacting moiety. The interactions may also vary with cell lines. By controlling/designing the surface chemistry of interacting materials, their internalization and ultimate fate/localization inside the cells can be controlled (localization inside lysosomes or escape inside the cytosol and/or further transport into sub-cellular compartments such as nuclei, mitochondria, etc.). We are checking the interactions of different materials such as quantum dots (with negative, positive and zwitterionic surfaces), polymer coated fluorescent nanoparticles, porous polymeric capsules (having different cargo inside the cores and various functionalities in the shell), drug loaded mesoporous materials, BODIPY-metalloid compounds, and liposomes, etc. with cell lines available in our laboratory. The surface chemistry of these materials play pivotal...
role in deciding their rate of internalization, localization and/or release of cargo at the destination point.

COLL 259

Correlating nanoparticle surface chemistry with antimicrobial activity via NMR techniques

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Surface chemistry of metal nanoparticles dictates many aspects of their behavior including charge transfer properties, toxicity, and stability. Here, we use several NMR techniques to elucidate the formation, stability and subsequent use of alloyed nanoparticles in antimicrobial applications. Specifically, we correlate ligand identity, quantity and arrangement with toxicity figures of merit such as IC50. These studies represent some of the first quantitative correlations between controlled metal ion release from alloyed nanoparticles and the role of nanoparticle ligand chemistry in that release.

COLL 260

Modeling of selenium nanoparticle formation and implications on bacterial and cellular responses

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Nanomaterials have a profound effect on cell-material interactions, including the prevention of bacterial proliferation and biofilm formation as well as heightened mammalian cell growth for tissue regeneration. Selenium nanoparticles (SeNP) have been synthesized as colloidal nanoparticles in solution as well as a coating for a variety of surfaces, including metals, paper products, and polymers to prevent bacterial adhesion and growth. Additionally, these coatings have been seen to be non-toxic to healthy cells while reducing the proliferation of cancer cells, such as osteosarcoma cells. To ensure precise and consistent SeNP coverage, we aim to tabulate several relevant aspects of the particle. By adjusting reaction parameters for producing SeNP, a variety of data can be collected and analyzed. Pertinent reaction characteristics include nanoparticle size and coverage, which in turn affects surface roughness and chemical reactivity. Thus, for the first time, a cubic response surface model was developed here using a central composite design (CCD), to predict SeNP coating and the resulting effect on cellular interactions. Nano-scale roughness is known to modify protein adsorption (and thus cellular response) onto the surface of a material. With this CCD
model, we can predict the changes in SeNP coverage according to our synthesis parameters, and better direct the cell-material interactions that result. We have seen decreases in bacterial adherence, proliferation and deposition of biofilm while at the same time improving healthy mammalian cell growth on these SeNP surfaces.

AFM of SeNP-PLLA synthesized with 5, 30 or 60 seconds (from left to right) of exposure to NaOH, which precipitates the SeNP.

**COLL 261**

**Heterogeneous particles to model dynamic cell/surface interactions**

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The dynamic adhesive interaction between cells and surfaces is studied here using a model system where micron-scale particles flow continuously in shear over an adhesive planar collecting surface. This scenario is inspired by the behavior of white blood cells flowing in and interacting with the surface of veins. Depending on the presence and type of cell adhesion molecules, the white blood cells may flow, roll, or arrest. In the microparticulate model of the current study, electrostatically-negative silica microspheres are modified by sparse amounts of cationic polymer that forms ~10 nm positively charged regions on the particle surface. Despite this modification the micro particles retain a net negative average charge. This model system adds functionality in a way that is heterogeneous and random like biological cells. Surfaces are engineered with polymers that act as artificial ligands and receptors to control the dynamic adhesive forces within the system. The adhesive interaction of these heterogeneous microparticles flowing past a silica flat is compared with the behavior of bare silica microspheres flowing over a collector containing analogous electrostatic heterogeneity. We report here that the location of the electrostatic patchiness (on the particles versus on the collector) can produce differences how particles and surfaces interact. In particular we identify compositions where if the functionality is placed on the
microsphere, no capture occurs, but if the functionality is placed on the planar collector, adhesion is observed. Differences are though to arise from the exposure of different regions of the surface from particle rotation.

COLL 262

Single molecule resolution of interfacial biomacromolecule dynamics

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Interactions between molecules and surfaces lead to complex and highly-varied interfacial behavior, where heterogeneity may arise from spatial variation of the surface/interface itself, from structural configurations (i.e. conformation, orientation, aggregation state, etc.), or temporally, through inhomogeneous dynamic behavior. As an example of temporal heterogeneity, we have used high-throughput single-molecule tracking methods to study the interfacial transport of small molecules, polymers, and biomolecules. We universally observe intermittent motion, with periods of confined Brownian motion punctuated by long (Levy) flights. The motion is described within the context of a continuous time random walk (CTRW) model, with power-law distributions of both waiting times and flight distances. CTRW-based search processes are widely predicted to exhibit improved efficiency compared with Brownian searches, and many biological systems have evolved intermittent search strategies. Using single-molecule Forster Resonance Energy Transfer, we have found that mobility based on this CTRW mechanism influences diverse behavior that relies on interfacial molecular searching and association, ranging from DNA hybridization to protein layer formation.

COLL 263

Super-resolution imaging of fluorescently-tagged ligands on gold nanoparticle surfaces

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Visualizing the precise location of individual ligands self-assembled on the surface of gold nanostructures is a distinct experimental challenge due to the small size of both the ligands and the gold particles relative to the resolution of most characterization techniques. In this talk, we will describe the use of super-resolution fluorescence imaging to determine the location of individual fluorophore-labeled thiolated DNA bound to the surface of gold nanoparticles. In super-resolution imaging, diffraction-limited emission is fit to a model function, such as a 2-dimensional Gaussian, in order to determine the location of the emitter with precision of 5-10 nm. By modulating emitters between emissive and non-emissive states, we are able to precisely locate a single fluorophore at a time, allowing us to build up an image of the location of individual
fluorescent dyes attached to the nanoparticle surface via the DNA linker. Using this technique, we map out the shape and orientation of the gold structure, while also gaining insight into the apparent surface binding of the DNA on the gold nanoparticle surface. Significant heterogeneity is observed across the nanoparticle population suggesting that our cartoon picture of monolayer DNA coverage on the surface of gold nanostructures is, in fact, an oversimplification of what is really happening at the nanoscale.

**COLL 264**

**Nanoscale insight into the impact of heterogeneous probe spatial distribution on surface hybridization**

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The binding affinity, selectivity and kinetics of surface-based DNA sensors and microarrays may be profoundly impacted by the nanoscale arrangement of immobilized DNA molecules (probes) on the surface. Recent high-resolution microscopy studies have shown that the DNA probes on DNA monolayers are often not uniformly distributed on the surface. Yet, the impact of heterogeneity of probe density on surface hybridization has been largely unknown. By directly visualizing single hybridization events on dynamic self-assembled monolayers and developing spatial statistical analysis, we have provided single molecule level evidence that the hybridization efficiency is impacted by the presence of neighboring probe molecules. A number of mechanisms may be at play, including steric hindrance and competition between the probe molecules for target molecules. Such molecular level insights into hybridization on surfaces may inform new strategies to engineer more robust and reliable DNA sensors.

**COLL 265**

**High-resolution, fast-scanning Atomic Force Microscopy for studying dynamic processes**

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Atomic Force Microscopy (AFM) has become a well-established technique for single molecule studies and even sub-molecular scale research. Several new developments in terms of faster AFM imaging and imaging modes, based on phase or frequency, have been established in order to decrease the cantilever response time and increase the AFM’s scan speed to open up exciting applications such as studies of molecular dynamics.
The combination of a flexure based tip-scanner and compact design allows for full integration of fast scanning AFM with advanced commercially available optical microscopy. Thus, AFM imaging of approximately 1 frame per second can be seamlessly combined with methods such as, fluorescence, confocal, TIRF, STED microscopy, to name a few. This enables the study of individual molecule dynamics using AFM and simultaneous optical microscopy.

Tip-sample interaction is minimized using cantilever oscillation amplitudes as low as 0.2 nm paving the way to sub-molecular resolution even on soft samples in liquid environments. Topographical images of membrane proteins, DNA-origami, and a dynamic biomechanical study of Bacteriorhodopsin (fig. 1) interacting with photons will be presented to corroborate this.

More than half a century after the first high-resolution electron microscopy images of collagen type I banding have been reported, we are now able to gain a high-resolution temporal insight into the dynamics of collagen I fibril formation and its characteristic 67 nm banding. To this day, literature abounds with conflicting data regarding the models of its fibril formation, structural intermediates, and kinetics. Fast-Scanning AFM is the only currently available high-resolution imaging technique to offer insight into the collagen I fibrillogenesis by operating in situ. The described technique will be instrumental for future studies of the structural dynamics of protein systems and other related events.

**COLL 266**

**Energetic basis for the molecular-scale organization of bone and enamel**

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The interactions between proteins and hydroxyapatite (HAP) are critical to an understanding of the biomineralization of mammalian hard tissues such as bone and teeth. The remarkable properties of bone derive from a highly organized arrangement of co-aligned nm-scale apatite platelets within a fibrillar collagen matrix. The origin of this arrangement is poorly understood and the crystal structures of hydroxyapatite (HAP) and the non-mineralized collagen fibrils alone do not provide an explanation. Moreover, little is known about collagen-apatite interaction energies, which should strongly influence both the molecular-scale organization and the resulting mechanical properties of the composite. We investigated collagen-mineral interactions by combining dynamic force spectroscopy (DFS) measurements of binding energies with molecular dynamics (MD) simulations of binding and AFM observations of collagen adsorption on single crystals of calcium phosphate for four mineral phases of potential importance in bone formation. In all cases, we observe a strong preferential orientation of collagen binding, but comparison between the observed orientations and TEM analyses native tissues
shows only calcium-deficient apatite (CDAP) provides an interface with collagen that is consistent with both. MD simulations predict preferred collagen orientations that agree with observations and results from both MD and DFS reveal large values for the binding energy due to multiple binding sites. These findings reconcile apparent contradictions inherent in a hydroxyapatite or carbonated apatite (CAP) model of bone mineral and provide an energetic rationale for the molecular scale organization of bone. Besides, in the case of enamel, the interaction between amelogenin and HAP (100) has been discussed to show that small changes in the primary sequence can result in significant changes in the protein-protein and protein-HAP interactions.

COLL 267

Phase inversion behavior of particle-stabilized emulsions and porous polymer preparation

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Emulsions stabilized by colloidal particles are called Pickering/Ramsden emulsions. One of the most important factors in stabilizing particle-stabilized emulsions is wettability of the particles against oil/water interfaces. Relatively hydrophilic particles preferably stabilize oil-in-water (o/w) emulsions, while water-in-oil (w/o) emulsions are formed by using relatively hydrophobic particles. The particle wettability can be controlled by chemical modification of the particle surfaces, addition of molecular surfactant, changes in pH and salt concentration and oil chemical structures, etc. The other significant factor is a volume fraction of water relative to the total volume ($\phi_w$). At a given particle wettability, emulsions show a phase inversion from w/o to o/w with increasing $\phi_w$. In this study, we have controlled “average particle wettability” by mixing two fumed silica particles with different hydrophobicity and changing the particle ratio (P.R.) for emulsions of water and oil consisting of styrene and divinylbenzene. The critical $\phi_w$ values at which a phase inversion takes place have been determined as a function of P.R. The phase inversion behaviour, summarized as phase inversion diagrams (plots of P.R. vs critical $\phi_w$), is dependent on protocols of emulsion preparation, showing the particle initial locations before emulsification significantly affects emulsion characteristics. Selecting $\phi_w$ and P.R. which give stable w/o emulsions with high internal phase, porous polymers have been prepared.

COLL 268

From phenomenon to formulation: Investigating excipients that enhance the stability of colloidal drug aggregates in biological milieus

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Numerous small molecules, including lead candidates and approved drugs, spontaneously and reversibly aggregate to form colloids at micromolar concentrations in aqueous solution. For early drug discovery, this self-assembly process can lead to false positive results in high throughput screening (HTS). Formation of such particles is governed by the critical aggregation concentration (CAC), which is in turn dependent on a variety of factors, including structure, ionic strength and pH. Approved drugs, including fulvestrant, sorafenib, and lapatinib, have shown substantially attenuated anti-proliferative effects in their colloidal forms as compared to monomeric formulations.

While the implications of colloidal formation are pervasive in early compound development, controlling this self-assembly process has proven to be far more challenging. Changes in particle size occur rapidly in high salt containing solutions, especially when formulated well above the CAC, making it difficult to examine their behaviour over time in biological systems. Though a universal means of stabilizing such promiscuous small molecules is difficult to envisage, further probing their intrinsic properties relies heavily on a clearer understanding of the aggregation process and how it can be tuned to meet such stability objectives. Here, we look deeper into the colloidal properties of several clinically used anticancer drugs in aqueous buffers and outline small molecule and polymer excipients that can be used to enhance colloidal stability at both higher salt and compound concentrations. Additionally, we utilize a mixture of light scattering and microscopy techniques to examine how colloid surface properties can be exploited to adsorb specific biomacromolecules. The outlined strategies thus provide a means to transition from unexpected assembly phenomenon to one exploitable for investigating the impact of colloidal aggregation in biological and materials science applications.

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Dispersant Interactions at Oil-Water Interface: Insights from Molecular Dynamics Simulation
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Dispersants play a crucial role in the suspension polymerization process for the production of polymer resins. The dispersant package used in industrial processes often involves a combination of two or more macromolecules (polymers or proteins). How these molecules behave at the oil-water interface is not very well understood, which hinders the development of new dispersant packages. In this study, we use the molecular dynamics modeling technique to simulate the activity of one dispersant package (gelatin and PADMAC) at the oil-water interface. These simulation results show that the charged amino acids in gelatin keep the gelatin at the interface while the non-polar region is immersed in the oil phase. The PADMAC polymer is not soluble in the oil phase and stays in the aqueous phase. Thus, PADMAC alone cannot function as a dispersant. Strong electrostatic interactions between the cationic backbone of PADMAC and the charged groups in the gelatin anchor the PADMAC to the gelatin and therefore to the interface. This shows that PADMAC, in conjunction with gelatin, can adsorb to the oil-water interface and thus stabilize oil droplets in the suspension polymerization process. These observations from simulation have been confirmed by our experiments. The fundamental understanding gained in this study has further helped the design of new dispersant packages for suspension polymerization.

COLL 270

Compatibilization of inorganic nanoparticles in polymer matrices by means of methacrylate based amphiphilic copolymers

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The incorporation of inorganic nanoparticles into polymeric matrices leads to enhanced mechanical stability, flame retardancy, scratch and UV resistance. In order to attain improved properties, it is essential to obtain a material where nanoparticles are homogeneously distributed. Such nanocomposites can be achieved by surface modification of the inorganic particles leading to high compatibility between the
nanoparticles and matrix. Therefore, we have developed two strategies applying methacrylate-based amphiphilic copolymers which strongly bind to the particle surface without the need for forming covalent bonds (fig.1). Strategy 1 utilizes multicomponent solvent mixtures consisting of immiscible water/organic solvents, which are converted to a monophase by the addition of ethanol, making the nanoparticle coating possible. Strategy 2 can be realized with the same polymer acting as emulsifier in an inverse emulsion. Within the droplets, inorganic nanoparticles are formed from precursor salts in a sol-gel like reaction. Introducing these particles in a polymer matrix can yield improved materials, which are analyzed by dynamic mechanical analysis (DMA) and nanoindentation. Binding strength is studied using isothermal titration calorimetry (ITC), the presence of primary particles is confirmed by dynamic light scattering (DLS) and scanning electron microscope (SEM).

Schematic drawing of the two different strategies to obtain nanoparticles coated with amphiphilic copolymers

**COLL 271**

**Star diblock copolymer concentration dictates the degree of dispersion of carbon black particles in nonpolar media: Bridging flocculation vs. steric stabilization**

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The solution behavior of a polystyrene-hydrogenated polyisoprene star diblock copolymer (Mn ~ 384 K; 6 mol % polystyrene) is examined in non-polar media. $^1$H NMR
studies in d_{25}-dodecane confirm that the outer polystyrene blocks are only partially solvated in \( n \)-dodecane at 25\(^\circ\)C: the apparent polystyrene content of 3.2 mol\% remains constant on heating up to 100\(^\circ\)C. Physical adsorption of this copolymer onto carbon black particles is studied, with particular attention being paid to the effect of copolymer concentration on colloidal stability. An adsorption isotherm is constructed using a supernatant depletion assay based on UV spectroscopy using the aromatic chromophore in the polystyrene block. Langmuir-type adsorption is observed with a maximum adsorbed amount, \( \Gamma \), of \( \sim 2.2 \) mg m\(^{-2}\). Analytical centrifugation, optical microscopy and transmission electron microscopy studies indicate that the star diblock copolymer acts as an effective flocculant at low concentration, with steric stabilization only being observed above a certain critical copolymer concentration (\( \sim 5.5 \) % w/w). This is attributed to the spatial location of the polystyrene block and the star copolymer architecture, which enables copolymer adsorption onto multiple carbon black particles at low coverage, leading to bridging flocculation (see Figure 1). Above 5.5 % w/w copolymer, the surface coverage is sufficiently high that all of the polystyrene ‘stickers’ adsorb onto single carbon black particles, resulting in colloidally stable, sterically-stabilized carbon black dispersions. Finally, small-angle X-ray scattering (SAXS) studies provide useful insights regarding the subtle changes in fractal morphology that occur with increasing copolymer concentration. Moreover, SAXS provides direct evidence for the presence of the copolymer at the particle surface.

**Figure 1.** Schematic representation of the two roles played by a star diblock copolymer in the presence of a model colloidal substrate in non-polar media: (a) bridging flocculant and (b) steric stabilizer.
Molecular Janus particles based on functionalized fullerenes: Precise synthesis and assembly in solution

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Since the concept of “Janus grains” was introduced by de Gennes in his Nobel lecture, tremendous attention has been paid on their symmetry-breaking structures, self-assembly behaviors, and unique properties. In this work, a series of molecular Janus particles based on functionalized fullerene with precisely-defined structures were synthesized. These Janus particles exhibit intriguing self-assembling behaviors in solution. Fully hydrophilic, carboxylic acid functionalized fullerenes (AC₆₀) behave as hydrophilic macroions in polar solvents by showing strong attractions with each other mediated from their counterions and consequently self-assembling into single-layer, hollow, spherical blackberry-type structures in solvents with moderate polarity. After breaking symmetry, the amphiphilic Janus particles composed of AC₆₀ tethered by one (AC₆₀-C₆₀) or two (AC₆₀-2C₆₀) hydrophobic C₆₀ yielded various micellar morphologies including spheres, cylinders and vesicles, depending on the molecular architectures and solvent polarity. Furthermore, uniquely hierarchical structures such as helical structures can be formed by the assembly of Janus particles deriving from conjugates of positively and negatively charged C₆₀.

Evolution of polymeric nanoparticles formation during condensation of hydrophobic alkoxysilanes in an organic solvent free sol-gel method

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Hydrophobic alkoxysilanes based polymeric nanoparticles can be used in different biomedical applications such as a carrier for biosensors and as a vehicle for delivering drugs. These nanoparticles also can be used to capture, encapsulate, and immobilize cells and biomolecules in the biological system. The formation of polymeric nanoparticles can occur simultaneously or after a certain period of time depending on the solution compositions, pH, and temperature. To understand the polymeric nanoparticles size evolution using the sol-gel method, two hydrophobic alkoxysilanes: n-propyltrimethoxy silane (nPM) and 3,3,3-trifluoropropyl methoxy silane (3F) were used. For this study an organic solvent free solution was used for the hydrolysis and for condensation process. Five different acidic pH conditions ranging from 1.7 to 4.0 were tested. The evolution of polymeric nanoparticles sizes was determined by Dynamic Light Scattering (DLS) for 1 hour to 72 hours as a continuous reading. Polymeric nanoparticles were also characterized using an Atomic Force Microscope (AFM). The DLS studies showed that as condensation progressed, polymeric particles continued to
evolve from a few nanometers to over micron sizes depending on specific experimental conditions. DLS observed nanoparticles sizes were later compared with the sizes observed in the images obtained from AFM. This study will help better understand and control growth of desired hydrophobic functional polymeric nanoparticles in an environmental friendly manner for their potential applications in biomedical applications.

**COLL 274**

**Anti-agglomeration Ni@yolk-ZrO₂ structure with sub-10 nm Ni core: Preparation, characterization, and catalysis in steam reforming of methane reaction**

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A novel two-step method to prepare well-separated nanoparticle catalysts with yolk-shell structure via double oxide coating and template removing was developed. This synthesis protocol is advantageous for the preparation of single core non-noble metal-based catalysts with small core size, high substrate permeability and sintering resistance. Ni@yolk-ZrO₂ nanoparticles with sub-10 nm Ni cores were synthesized via a double-template method. Ni@SiO₂ colloids prepared in a water-in-oil microemulsion and subsequent encapsulation with silica was coated with 7 nm thickness of zirconia. Following base-removing of SiO₂ lead to a well-separated yolk-shell structure. Size of Ni cores in the shells was effectively controlled at 5.6 nm in average for high active surface area. Active Ni particles agglomerating behaviour was controlled by tuning the total pore volume and micropores of the zirconia hollow shell. The Ni@yolk-ZrO₂ showed surprisingly high activity and sintering resistance on steam reforming of methane at 750 °C, attributed to its nano-size Ni particles remaining inside zirconia hollow shell. Relevant characterization using XRD, TEM, TG/DTG, SEM, EDX and ICP-OES was conducted. The remarkable anti-agglomerating property of the yolk-shell structure finds its application in extension to other active metals and high temperature reactions.

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Interface bonding effect between ternary sulfide solid solution and TiO2NTs composite by solvothermal synthesis

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Ternary sulfide solid solution @ TiO2NTs composites synthesized by a two step process of anodization and solvothermal methods present a Ti-S bonding effect and enhanced visible light responsibility, which shows great practical potential in the photocatalytic application for hydrogen production. The aim of this work is to investigate the effects of the crystal forms of TiO2NTs, the amount of doped Ag, and other doped elements on the bonding effect between ternary sulfide solid solution and TiO2NTs through Raman spectra analysis. The results show that there is a strong Ti-S bonding effect between anatase TiO2NTs and ZnS-In2S3-Ag2S and the bonding degree is improved with the amount of anatase TiO2. The increase of Ag content strengthens the bonding effect between ZnS-In2S3-Ag2S and TiO2NTs. However, the excessive Ag⁺ leads to the formation of the mixture of ZnS-In2S3 and Ag2S instead of ZnS-In2S3-Ag2S and the Ti-S bonding effect disappears correspondingly. Cu²⁺ and Ni²⁺ can replace Ag⁺ to form ternary sulfide solid solution, and the Ti-S bonding effect with TiO2NTs is also found which is strengthened in the following order: Cu²⁺ >Ag⁺ >Ni²⁺. Also, UV-vis DRS spectra were studied to investigate the photoabsorption property of the ternary solid solution @ TiO2NTs. The Ti-S bonding effect between ternary sulfide
solid solution and TiO2NTs can give rise to the red shift of the absorption edges of the samples and the extent of the red shift is increased with the improvement of the Ti-S bonding effect. Among Cu2+, Ag+ and Ni2+ doped samples, the red-shift extent of the absorption edge is increased in turn.

COLL 276

Back to basics: Is complete transmetallation within metal-organic frameworks simple and feasible at room temperature?

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Metal-organic frameworks (MOFs) has emerged as a novel class of inorganic-organic hybrid materials in recent decades. A rapid development of MOFs have been experienced on their potential applications, such as gas storage and separations, chemical sensing, drug delivery, and catalysis. These highly crystalline and porous material are tunable on the atomic level by judicious of designed and functionalization. Post-synthetic metal metathesis has potentially enhance the ease of functionality of the MOFs. Current knowledge about metal exchange studies in MOFs is still dark in the box, especially for a complete metal exchange. In our studies, two magnesium MOFs were used as the parent MOFs to evaluate the influence of solvent, linker, pore size and metal units. After metal exchange these two magnesium-based MOFs with other transition metals, the degree of exchange and crystallinity of the corresponding MOFs varies based on the nature of target metals. Under consideration of the effect of several key, the “FLEG” prerequisites was proposed for complete transmetalation. Following the “FLEG” prerequisites, a series of isostructural MOFs were synthesized. The “FLEG” prerequisites provide some fundamental knowledge about the metal exchange process at room temperature, which surely benefit the application-directed synthesis of MOFs.

COLL 277

Self organization of oligopeptides: From molecules to fibriles to spheres

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Oligopeptides have been recognized as promising building blocks both in materials and life sciences. Among others Diphenylalanine (FF) and its derivatives such as the Fmoc terminated Diphenylalanine (FmocFF) are of major interest. The pH triggered self assembly of FmocFF into fibrillar gel networks results in materials relevant in tissue engineering while self organized diphenylalanine organizes in a variety of mesostructures that are of interest in materials science. These include nanotubes, ribbons, fibrils etc. Under appropriate conditions the pH triggered self organization of
diphenylalanine into ultrathin fibrillar networks generates gels that are suitable for TEM diffraction experiments. Based on these experiments a structural model could be proposed (1) that meanwhile has been proved (2) and refined (3) by xray experiments. The chemical cleavage of Fmoc groups from the "as geled" fibrillar networks results in characteristic morphological changes from fibrilar into globular networks (fig.1A). Based on morphological data a model for the transformation within the gels will be discussed. The formation of the spherical structures is assumed to be related to a nucleation and growth of Diphenylalanine assemblies (fig.1B) within the poreous network of FmocFF. The growing nuclei finally desintegrate the original fibrilar gel structure while forming a new particles gel structure.

(1) H.-G. Braun et. al. Braun, Colloids and Surfaces B: Biointerfaces 2012, 97, 43–50
(3) J. Raeburn et. al. Soft Matter, 2015, 11, 927-935

Fig.1
A) Spherical structures embedded in a gel mesh (FmocFF)
B) Spherical nuclei of stiff needle like assemblies

**COLL 278**

**Micelle-polyelectrolyte complexation in buffered aqueous solution**

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We report the synthesis and characterization of poly(dimethylaminoethyl methacrylate)-b-poly(styrene) block copolymers and their complexes with a model polyanion. The polymers, synthesized by RAFT polymerization, have narrow molecular weight distributions ($D < 1.13$) and form uniform spherical micelles with pH- and ionic-strength responsive coronas in aqueous buffers. We characterize complexes of these micelles with poly(styrene sulfonate) via dynamic light scattering and cryogenic transmission electron microscopy, and show that the complexes exhibit multimodal size distributions that evolve on timescales of days to weeks at physiologically relevant ionic strengths. We discuss the thermodynamics implied by these results and implications for the design of gene- and drug-delivery vehicles using these types of interpolyelectrolyte complexes. Finally, we discuss initial studies of complexation with polycationic micelles of more complex architectures that may enhance complex solubility and stability for future biological applications.

**COLL 279**

**Polymer brush colloidal particles as building blocks for functional materials**

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We used polymer brush nanoparticles (PBNPs) to prepare functional materials suitable for ultrafiltration, and proton and lithium ion transport. The nanoparticles used to assemble the ultrafiltration membranes were prepared by first modifying their surface with 2-bromoisobutyrylbromide (ATRP initiator). The pSPM-r-pEEMA, pDMAEMA-r-pMMA, pSPM, pHEMA, pHEMA-r-pSPM and pSPM-r-pEEMA brushes were grown on the surface of silica particles using surface initiated atom transfer radical polymerization (SI-ATRP). The membranes prepared from these colloidal particles can be assembled and re-dispersed in solution by switching the solvent. We prepared two types of reversible membranes: membranes made of silica modified with polymer brushes carrying acidic and basic groups, and membranes in which the grafted polymer brushes have neutral groups. The former are stable in most organic solvents and easily dissolve in water, while the latter are water-stable and capable of dispersion in organic solvents. Both types of membranes are nanoporous and capable of size-selective transport and ultrafiltration.

We also prepared proton conducting membranes using silica nanoparticles (SNPs) surface-grafted with 40-400 nm sulfonated polymer brushes, poly(3-sulfopropylmethacrylate), pSPM, and poly(4-styrenesulfonic acid), pSSA. The membranes prepared from the NPs carrying longer polymer chains possessed polymer-like characteristics, compared to the stiffer membranes made with shorter polymer brushes. All these membranes showed comparable proton conductivities, with a maximum value of $\sim 0.06$ S/cm at 98 °C and 70% R.H. Finally, lithium conducting membranes were prepared using 500 nm SNPs surface-grafted with PEO-containing polymer brushes, poly(ethylene glycol) monomethyl ether methacrylate, PEGMA, and with poly(ethyl methacrylate), PEEMA. The membranes prepared from the NPs carrying longer polymer chains possessed polymer-like characteristics, compared to the stiffer membranes made with shorter polymer brushes.
There materials showed high ionic conductivity and unusual conductivity temperature dependence. Specifically, their conductivity was relatively low (~0.8 mS/cm) at 4 °C, increased to ~2.5 mS/cm in the range of 40-80 °C and decreased to ~1.0 mS/cm around 100 °C. We attribute this behavior to the temperature-responsive properties of PEGMA and PEEM brushes.

COLL 280

Estimation of crystal nucleation barriers in colloid-polymer mixtures

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A colloid-polymer mixture in equilibrium in a finite volume \( V \) with particle number \( N \) at a density exceeding the onset density of freezing may exhibit phase coexistence between a crystalline nucleus and surrounding fluid. Using a computational method suitable for the estimation of the chemical potential of dense fluids we obtain the excess free energy due to the surface of the crystalline nucleus. While our analysis is appropriate for crystal nuclei of arbitrary shape, we find the nucleation barrier for a soft version of the effective Asakura-Oosawa model to be compatible with a spherical shape, and consistent with classical nucleation theory [1]. In this context we will also discuss a novel (ensemble-switch) method for the determination of interfacial tensions between liquid and crystal interfaces [2].


COLL 281

Using smart polymers to regulate DNA-mediated nanoparticle assembly, crystal formation, and interparticle spatial properties

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In this presentation we describe our recent work related to using temperature responsive polymers to regulate DNA-mediated interactions at nanoparticle interfaces (Hamner et. al. ACS Nano 2013, 7, 7011). In this work a series of thermo-responsive pNIPAAm-co-pAAm polymers have been synthesized with low critical solution temperatures (LCST) ranging from 37-65 °C. These polymers have been co-grafted onto nanoparticles containing single stranded oligonucleotides (ssDNA). The thermo-responsive behavior of the polymer allowed for regulating the accessibility of the sequence-specific hybridization between complementary DNA functionalized AuNPs, leading to controllable assembly kinetics, unique morphology and new phase behavior. This presentation will also describe recent synchrotron small angle X-ray scattering (SAXS) studies that probed the assembled crystals thermal response and phase
behavior. The role that DNA length and structure, as well as polymer conformation plays in the observed properties will be discussed. We thank the AFOSR for support of this work (FA9550-10-1-0033).

COLL 282

Directing the colloidal assembly of patchy spheres by capillary interactions

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Directing the assembly of building block colloidal particles is key to the fabrication of multiple classes of new materials. Here we present a simple single step approach for on-demand assembly of colloidal clusters. We direct the assembly of microparticles by fluid induced capillary interactions. Polystyrene microspheres can be designed to have discrete iron surface patch(es) of controllable size and shape. The iron-coated surface develops an oxide skin when dispersed in water containing fatty acid salts. The strong affinity of \( n \)-alkanoic fatty acids for iron oxide can be used for its selective condensation on the oxidized metal patch. The liquidity of the condensed fatty acid patch makes the particle stereoselectively sticky and leads to their self-assembly into discrete clusters. We study the kinetics of the assembly process as the function of relative surface patch area \( f \). We find that Janus spheres \((f = 0.5)\) typically assemble into tetramers with tetrahedral geometry. However, triplets and doublets are predominantly assembled upon decreasing the patch size to \( f = 0.2 \) and 0.15 respectively. This change in the self-assembly behavior can be attributed to the decrease in the lipid-lipid shell overlap area upon decreasing the patch size. The assembly process was theoretically investigated by Mote Carlo simulations, where the patch-to-patch interactions are modeled on the basis of square-well sticky potential. The experimental observations of equilibrium cluster morphology and the kinetics of the process are in excellent correlation with the simulations (Figure 1). This fatty acid based capillary binding offers an unconventional way of assembling microparticles into ordered clusters and can be used to organize structures at any length scale in a simple and robust manner.
Membrane mediated assembly of chiral colloidal rafts

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Inclusions distort local membrane structure leading to membrane-mediated interactions that are fundamentally different from well-studied bulk interactions, yet are difficult to experimentally measure. We investigate liquid-liquid phase separation in a highly simplified system of colloidal membranes. The bulk phase separation of dissimilar rods is inherently unstable and gives way to formation of finite-sized, highly-monodisperse colloidal rafts. Using single molecules techniques we measure kinetics by which thousands of rods assemble into an isolated raft. Subsequently, we quantify repulsive raft-raft interactions and correlate them to raft-induced membrane distortions; demonstrating that particle chirality is an essential requirement for raft formation. At high densities rafts assemble into cluster crystals which constantly exchange rods with the membrane background to robustly maintain a self-limited size. Finally, we demonstrate raft polymorphism by forming supra-rafts, 2D liquid droplets with complex highly non-spherical shapes such as a beads-on-a-string polymer.

Figure 1 (a) A micrograph showing the near equilibrium self-assembled state of Janus microspheres ($f = 0.5$) in the presence of fatty acids. (b) A snapshot of the Monte-Carlo simulations showing the formation of discrete clusters of the Janus spheres. The simulation data exhibit excellent correlation with experimental results.
COLL 284

Directional self-assembly of polymeric colloids

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The introduction and exploitation of directional supramolecular interactions within colloidal self-assembly has the potential to fabricate open 3D architectures that can function in applications ranging from photonics and plasmonics to biomaterials and catalysis. The use of colloidal self-assembly as a potent bottom-up technique to construct materials is motivated, in part, by the utility of colloidal particles as highly tunable inexpensive platforms that exhibit unique long- and short-range order, as well as multiple specific orientations. As such, colloidal self-assembly is dynamic and offers the potential for modular fabrication, resulting in well-defined and diverse structures and/or morphologies (e.g., clusters, crystals, chains) via simple modification of intermolecular interactions. While the vast majority of colloidal assemblies have been limited to either non-directional self-assembly or DNA hybridization as a key feature, we have expanded our approach to investigate other supramolecular elements based upon directional self-assembly. In this presentation, we will introduce methodologies based upon directional interactions to achieve open colloidal lattices using patchy particles. In particular, we will introduce host/guest interactions to facilitate open colloidal lattices.

COLL 285

Probing the solid/gas and solid/liquid electrochemical interfaces using in situ/operando ambient pressure X-ray photoelectron spectroscopy

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The interaction of a catalyst and its operating environment occurs at an interface between two-phase boundary at given temperatures and pressures. These interfaces
play an important role in for a wide range of catalytic reactions and extending even towards electrochemistry. Where two and even three-phase boundaries between catalysis/electrode, electrolyte, and gaseous fuel, are also exposed to applied potentials and the transfer of current. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to water splitting have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. The ability to study these interfaces has proven to be difficult and is only further exacerbated by the limited number of techniques capable of operating under \textit{in situ/operando} environments. To overcome these challenges, we use \textit{in situ/operando} ambient pressure X-ray Photoelectron Spectroscopy (APXPS). APXPS is a photon-in/electron-out process that can provide both atomic concentration and chemical specific information at pressures greater then 1 Torr. Using synchrotron X-rays at Lawrence Berkeley Nation Laboratory, the Advanced Light Source and the endstation is outfitted with various \textit{in situ/operando} features such as heating to temperatures > 500 °C and electrical leads to support applying electrical potentials supports the ability to collect XPS data of an actual electrochemical devices while its working in near ambient pressures. This talk will provide several examples of catalysis and electrochemistry \textit{in situ/operando} APXPS studies that have been probed the solid/gas and solid/liquid interfaces.

**COLL 286**

**Structural evolution of an intermetallic Pd-Zn catalyst selective for propane dehydrogenation**

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A Pd-Zn alloy supported on Al\(_2\)O\(_3\) is a selective catalyst for propane dehydrogenation. In situ synchrotron X-ray diffraction (XRD), diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) and extended X-ray absorption fine structure (EXAFS) were used to follow the structural changes with increasing reduction temperature. EXAFS shows that a bimetallic nano-particle forms at about 230°C and the number of Pd-Zn bonds increases with reduction temperature. DRIFTS shows a change from bridge to linear bonded CO at 230°C; while there was little change in the surface of the nanoparticles when reduced above 325 °C. XRD indicates that the $\beta$\(_1\)-PdZn intermetallic alloy forms at reduction temperatures as low as 230 °C, likely first at the surface, but does not form extensively throughout the bulk until 500 °C. The improvement in the propane dehydrogenation selectivity is suggested to be due to isolation of the active metallic Pd atoms by inactive metallic Zn atoms.
Alloy catalysis across composition space: Elementary steps in hydrogenation reactions

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Alloy catalysis studies that span alloy composition space comprehensively are made possible by the combination catalyst libraries and multichannel microreactors arrays that allow parallel study of the catalytic activity of many catalysts compositions. Alloy catalyst libraries are prepared in the form of composition spread alloy films (CSAFs) of either two or three components. These alloy films have composition gradients parallel to their surfaces such that they expose a continuous regions of alloy composition space (Au$_x$Cu$_y$Pd$_{1-x-y}$, $x = 0 \rightarrow 1$ and $y = 0 \rightarrow 1-x$). These CSAFs can be characterized by a variety of spatially resolved bulk and surface analysis methods to map characteristics such as electronic structure, surface composition, and bulk structure across composition space. These can then be correlated experimentally with functional properties of interest. For studies of catalytic activity across composition space a 100 channel microreactor array has been fabricated that allows parallel measurement of steady state reaction kinetics over a wide range of reactant pressures and catalyst temperatures at 100 different alloy compositions. This has been used for studies of the kinetics of several of elementary surface reaction steps in the mechanisms of ethylene and acetylene hydrogenation on Au$_x$Cu$_y$Pd$_{1-x-y}$ and Ag$_x$Pd$_{1-x}$ CSAFs. Microkinetic models parameterized with temperature dependent rate constants are used to extract estimates of the barriers to elementary steps that can now be represented as functions of alloy composition. These barriers can then be correlated to alloy electronic structure as measured using UV and x-ray photoelectron spectroscopies.

Unraveling the relationship between structure and activity using model catalysts under near-ambient pressures

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The catalytic importance of metal–oxide interfaces has long been recognized, but the nanoscale determination of their properties and role is only now emerging. Atoms with
properties ranging from metallic to ionic are available at the metal–oxide interface and create unique reaction sites. To obtain a full picture of the morphological and chemical changes during model catalytic studies, X-ray photoelectron spectroscopy (XPS) experiments, from ultrahigh vacuum to near-ambient pressure (NAP) conditions coupled with theory, are presented to provide insight into the correlation between activity and model catalyst structure. The activation of an efficient associative mechanistic pathway for the water–gas shift reaction by an oxide–metal interface leads to an increase in the catalytic activity of ceria nanoparticles deposited on Cu(111) or Au(111) by more than an order of magnitude. In situ NAP-XPS experiments demonstrate that a carboxy species formed at the interface is the critical intermediate in the reaction. To obtain a complete picture of the morphological and chemical changes occurring during catalytic processes, we investigated the reduction of Cu₂O/Cu(111) under NAP of CO by a combination of in situ scanning tunneling microscopy (STM) and XPS to provide insight into the highly reducing environment of the water gas shift reaction on a model oxide surface. Systematic studies allow us to identify intermediate structures and determine how reaction fronts propagate across a surface with atomic scale resolution. Traditionally, STM is used to monitor surface structures and electronic properties, but here we show the surface oxide species can be identified with atomic-scale detail under near ambient pressures.

COLL 289

Characterizing a new class of catalysts based on MOF node chemistry

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Mesoporous metal-organic frameworks (MOFs) based on tetra-carboxylated linkers and hexa-zirconium(IV) oxo/hydroxy/aqua nodes are unusually chemically and thermally stable. The eight-connected nodes present numerous potential reaction and/or substitution sites. These properties, together with the high Lewis acidity of Zr(IV), make the nodes attractive as catalysts, either in their native form,¹ or after vapor-phase metalation.² For condensed-phase catalysis, especially hydrolysis, the proton topology of the node and its complex Bronsted acidity are defining factors. For gas-phase reactions, knowledge of the oxidation-state, atom siting, and local coordination of added transition metals is key to understanding catalytic activity and catalysis mechanisms. Because the catalytic clusters comprising nodes and subsequently installed metal atoms are monodisperse, both coordinatively and in terms of cluster size, the resulting ensembles are amenable to structural and functional characterization with a level of precision previously associated mainly with single crystal metal or metal-oxide surfaces. The porosity of the MOF scaffold, however, makes the catalyst arrays three-dimensional and greatly increases the number of active sites relative to two-dimensional arrays. In addition to boosting overall catalytic activity, the presentation of monodisperse catalysts in 3D rather than 2D arrays greatly facilitates structural and functional characterization. This presentation will focus on catalyst characterization, including in operando characterization. The characterization methods include DRIFTS, EXAFS, total X-ray
scattering and pair-distribution-function analysis, and energy-dispersive microscopy. Both structural characterization and functional characterization are facilitated by comparative computational modeling and simulations.


**COLL 290**

Ex situ and in situ characterization of plasmonic photocatalysts for solar fuel generation

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Our results have shown that incorporation of a plasmonic metal to a semiconductor can significantly improve the photocatalysis efficiency. This presentation shows our effort to ex situ and in situ characterize the band structure and the charge transfer processes in the plasmonic metal-semiconductor heterojunction photocatalysts. The transient absorption spectroscopy has been performed both in the dark and under light illumination to clarify the plasmon-enhanced photocatalysis mechanism. The in-situ X-ray absorption near edge structure (XANES) analysis reveals the correlation of the band structure with the charge transfer and the energy transfer processes in the plasmonic metal-metal oxide heterojunction photocatalysts.

**COLL 291**

Surface plasmon spectroscopy of nano sized metal particles

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Surface plasmon behaviour in nanoscale colloid systems continues to be an area of active research. In this talk I will summarise some of our recent work on 3 areas of surface plasmon spectroscopy. In the first part, I will discuss the use of surface plasmon spectroscopy for studying chemical reactions on the surfaces of single nanocrystals. Our aim here is to see whether spectroscopic methods can allow us to screen particles...
as catalysts and to uncover more information about the dissociation of gases and reactants on the surfaces of nanoscale materials. This builds on work on redox reactions on metal particles from 1996 [1]. In the second part, I will look briefly at surface plasmon coupling between dyes and metal particles using silica as a spacer [2]. In the final part I will look at some potential applications of surface plasmon effects including optical switches and plasmonic solar cells.

References

COLL 292

Silica coating and other coating shells

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This talk will attempt to provide an overview of different coating materials that have been applied to the encapsulation of nanoparticle colloids. Ranging from silica with various degrees of porosities, through smart polymers and multicomponent shells, such coatings have been crucial toward the analysis of nanoparticle properties, as well as many of the applications that are currently under development.

COLL 293

Metal-organic frameworks for gas separations: Using fundamental experimental studies and molecular modeling to highlight features of interest and optimized material

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Metal-Organic Frameworks (MOFs) are porous coordination polymers which have brought together the worlds of coordination chemistry and porous materials science. These materials, where metal oxide centres are linked through rigid multidentate organic moieties to give 3-D porous networks, have shown promise in areas including catalysis, drug delivery and adsorption/separation. As the spectrum of chemistries that can be incorporated into these materials is vast, the spectrum of properties is also extremely broad. It can thus be a difficult task to know which materials to concentrate on for further study. Fundamental adsorption studies, associated with the use of complementary techniques can be of interest in order to develop simple structure-property relationships. As so many MOFs have been made available, simple screening strategies can be of interest. However the data treatment is not simple as one would like to extract the most
relevant parameters for any potential application and be able to compare materials of different natures (zeolite, active carbons, MOFs ..). Here the use of adsorbent performance indicators can help. Depending on the separation considered, two categories of MOFs seem to distinguish themselves: those with small pores, and those with open metal sites.

In both of these cases, relatively strong adsorbate-adsorbent interactions occur. The use of microcalorimetry can be of interest to follow the extent of interactions. In the case of materials with specific open metal sites, it is possible to develop simple predictive models.

Further to this, molecular modelling can give great insights into the microscopic adsorption mechanisms that occur. This is particularly the case with small pore MOFs. Molecular modelling can be further used to screen for potentially interesting materials that have so far not been synthesised. If made in an intelligent manner, this can decrease the time from materials discovery to potential application.

Finally, the experimental data that has been accumulated so far can be compared to molecular modelling in order to develop simple structure-property relationships. These can be used to help us understand which properties may be most desirable for a specific separation.

This communication will highlight the various points made above.

**COLL 294**

**Microgels: Simple matter where complexity matters**

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Multi-sensitive, “smart” microgels display a variety of properties that distinguish them from colloidal particles as well as from (hyper-)branched polymers. The swelling of the soft microgels can be controlled via the chemical composition as well as the morphology of the particle. The size can respond to variations, e.g., of temperature, pH, pressure or solvent composition. The porosity of the microgels allows for the uptake and release of guest species.

Hollow responsive microgels are particularly promising materials. The stimuli-sensitive void size, shell thickness and permeability are of outmost relevance for the design of new, functional vehicles. We quantitatively study hollow nanogels at different states of swelling by Small Angle Neutron Scattering and demonstrate the structure-sensitivity dilemma: hollow nanogels with a slightly cross-linked shell reveal distinct sensitivity but possess nearly no void and are thus hardly “hollow”. Nanogels with a stiff shell are indeed hollow but less temperature-sensitive.[1] The concept was extended to develop unique doubly temperature responsive hollow microgels with individually tunable properties on the particle inside and outside.[2]

The behaviors of microgels at fluid, oil-water interfaces are distinctly different from that of common colloids.[3,4,5] It is possible to prepare emulsions the stability of which can be switched enabling new opportunities in biocatalysis.[6]

The interaction of pH-sensitive microgels at such interfaces was investigated by
compression isotherms. Surprisingly the microgels are easier to compress when they are in the charged as compared to the uncharged state. Thus the microgel-microgel interaction is not governed by direct Coulomb repulsion. [7] This demonstrates the distinct differences of soft microgels as compared to rigid colloids.


COLL 295

Zwitter surfaces and zwitter solids

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Langmuir has published extensively on the modification of surfaces with monomeric and polymeric zwitterion functionality. Zwitterions are known to interact only weakly with solution species, reducing or preventing nonspecific fouling. Nonfouling or nonadhesive surfaces are sought for coating articles (e.g. implants, contact lenses) in contact with biological fluids or synthetic materials exposed to the environment (e.g. membranes, ship hulls). This talk will summarize our contributions to stabilizing colloidal dispersions of nanoparticles with zwitterions. It will also focus on the mechanism for the action of zwitterions, evaluating both 2-dimensional and 3-dimensional zwitterionic barriers. The effectiveness of “PEGylation” for surface passivation will be compared with that of “zwitteration.”

COLL 296

Personal views on Langmuir as a reader, author, reviewer, editor, and EIC

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I published my first article in Langmuir in 1989 as a research scientist in the Xerox Research Center of Canada.1 It dealt with a topic of practical importance, but, somehow, my colleague A. Paine and I managed to publish part of our industrial work in the open literature! It was not easy and marked a turning point in my scientific career!
Reflecting back on this time brings me in close contact with young scientists who submit their first manuscript to *Langmuir*. Throughout my career, I have included *Langmuir* in my scientific life. I have now the privilege to be the Editor-in-Chief of *Langmuir*! Numerous challenges lie ahead, now is the time to build on *Langmuir*’s roots that have grown over the last 30 years throughout the world and across disciplines.

In this presentation I will discuss the current scope of Langmuir and what I see as the future focus of Langmuir, an issue of great importance not just to me, but also the entire editorial team, the members of our editorial board and of course our readers.


**COLL 297**

**Impacts of gold nanoparticle charge and ligand type on surface binding and toxicity to gram-negative and gram-positive bacteria**

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Although nanomaterials facilitate significant technological advancement in our society, their potential impacts on the environment are yet to be fully understood. In this study, two environmentally relevant bacteria, *Shewanella oneidensis* and *Bacillus subtilis*, have been used as model organisms to elucidate the molecular interactions between these bacterial classes and Au nanoparticles (AuNPs) with well-controlled and well-characterized surface chemistries: anionic 3-mercaptopropionic acid (MPA), cationic 3-mercaptopropionic acid (MPNH₂), and the cationic polyelectrolyte poly(allylamine hydrochloride) (PAH). The data demonstrate that cationic, especially polyelectrolye-wrapped AuNPs, were more toxic to both the gram-negative and gram-positive bacteria. The levels of toxicity observed were closely related to the percentage of cells with AuNPs associated with the cell surface as measured *in situ* using flow cytometry. The NP concentration-dependent binding profiles were drastically different for the two bacteria strains, suggesting the critical role of bacterial cell surface chemistry in determining nanoparticle association, and thereby, biological impact.

**COLL 298**
Investigation of effects of adsorption and immobilization onto silica nanoparticles on antimicrobial activity of Cecropin P1 and Cecropin P1C

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Antimicrobial peptides (AMPs) belong to a class of relatively short peptides family that have the ability to penetrate the cell membrane, form pores which eventually lead to cell death. Cecropin P1 (CP1, sequence SWLSTAKKLENSAKKRLSEGIAIAIQGGPR), an AMP with 31 amino acids and with a net positive charge of 5, was found to exhibit much higher antimicrobial activity against Gram-negative bacteria *E. coli* O157:H7 EDL933 compared to Gram-positive bacteria *Listeria monocytogenes* F4244. The minimum inhibitory concentration (MIC) of CP1 against *E. coli* O157:H7 EDL933 was 3.125 μg/well and exhibited the same antimicrobial activity against *E. coli* O157:H7 EDL933 when adsorbed onto silica nanoparticles. This was found to be consistent with preservation of α-helical secondary structure of CP1 upon adsorption as indicated by circular dichroism (CD) and molecular dynamics (MD) simulation. C-terminus cysteine modified Cecropin P1 (CP1C) was chemically immobilized onto silica nanoparticles with a Maleimide-PEG-NHS Ester linker of molecular weight 2000. The secondary structure of tethered CP1C as characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Circular Dichroism (CD) was found to be the same as that of CP1C in solution and adsorbed. However, tethered Cecropin P1C exhibited much lower antimicrobial activity against *E. coli* O157:H7 EDL933 compared to those in solution and adsorbed. The interactions of 3:1 DOPC/DOPG mixed membrane (mimic of bacterial cell membrane) as well as DOPC pure membrane (mimic of mammalian cell membrane) with free CP1C and CP1C tethered with (PEO)₃ linker were characterized using all atom molecular dynamics simulation and results compared with experiments.

COLL 299

Chitosan-based polymeric nitric oxides: Preparation, characterization, and antimicrobial effects

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In this study, we developed a new approach in the preparation of chitosan-based polymeric nitric oxides.

Commercial chitosan was cast into films from acidic aqueous solutions (UN-CS film). Glutaraldehyde reacted with UN-CS to introduce aldehyde groups onto chitosan film.
(GA-CS film). GA-CS reacted with a small molecule NO donor NOC-18, to covalently immobilize NO releasing moieties onto the polymer (NO-CS film). NO-CS could release NO for up to 3 hr at 37°C in PBS.

The released NO provided potent antimicrobial effects against both Gram-positive and Gram-negative bacteria, inactivated bacteria growing in biofilms, and showed synergistic effects with common antibiotics.

At 4°C, the NO-CS could be stored for more than one month without significantly losing NO releasing capabilities. Furthermore, NO-CS showed excellent biocompatibility with mammalian cells. All these attractive properties of NO-CS pointed to great potentials of the new materials for a wide range of biomedical applications.

**COLL 300**

**Surface grafted polymers for microarray platforms and understanding biochemical interactions**

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There is an urgent need for new technologies to detect and probe bacterial infection and carbohydrate arrays (glycoarrays) have gathered significant interest for this purpose. These arrays are important research tools in probing the mechanisms of bacterial, viral and toxin adhesion and in the development of new treatments for such infections. At the start of the infection process, for example by cholera toxin, HIV or *E. coli*, pathogens adhere onto the host cells, commonly through protein-carbohydrate interactions. Probing these interactions can be efficiently achieved by the presentation of carbohydrates in an array format, which can detect bacteria and provide structural information on their adhesion proteins and carbohydrate specificities.

Combining glycoarray technology with stimuli-responsive polymer surface coatings can provide a route to higher resolution arrays and the ability interrogate whole bacteria, whilst reducing non-specific binding and therefore minimising false positive outputs. We have previously described new and versatile methodologies to functionalise glass and silicon substrates with carbohydrates, producing arrays which are as simple as self-assembling on gold, but with the cost saving of working on glass and silicon. This work now includes the immobilisation of both RAFT-synthesised switchable non-fouling polymers using ‘click’ type reactions and libraries of glycopolymers, synthesised through tandem post-polymerisation modification methods. The arrays have been characterised by ellipsometry, quartz crystal microbalance with dissipation, drop shape analysis and X-ray photoelectron spectroscopy and their efficiency for facilitating protein-carbohydrate interactions whilst reducing non-specific protein adsorption has been investigated.
Sequence-specific peptoids for the molecular design of antifouling brushes and biointerface

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Antifouling brushes that resist non-specific protein- and cell-surface interactions can significantly improve the performance of an array of biomedical devices, and zwitterionic polymer brushes have captured significant recent attention. However, the development of their full potential has been hampered by a lack of chemical models to identify the molecular features conferring antifouling properties. Poly(N-substituted glycine) “peptoids” are a novel class of sequence-controlled, peptidomimetic polymers. We present surface grafted peptoids as an investigative platform offering precise control
over a range of relevant molecular features that may be difficult to simultaneously control with other systems. A targeted library of zwitterionic peptoid brushes with a range of charge arrangements and spatial separations was evaluated with an extended series of protein adsorption and mammalian and bacterial cell attachment measurements. We show that surface hydration and surface charge can be precisely tuned through the peptoid sequence design, that the charge separation can in some cases control the interactions with proteins, and that specific sequences may confer subtle differences in antifouling properties. We also precisely controlled for the grafted chain density and chain length, and our data indicate the dominant roles of these features in determining the performance of antifouling polymer brushes. Nonetheless zwitterionic brushes could offer advantages such as further chemical functionalization through some of the acid or basic groups. Further analysis of the cell attachment assays also shows an optimum level of protein adsorption for promoting cell adhesion and spreading. Overall our results indicate that the highly tunable nature of peptoids may be fruitfully applied to tailoring biointerfaces.
encapsulated in the surface (Adv. Mater., 2013, 36, 5029). It is very important that cells (bacteria, fibroblast and preosteoblast) behavior onto the surface is self-regulated (Adv. Mater., 2012, 24, 985) by their metabolism. We develop flat and curved metal (in particular titanium) surfaces with such properties as controlled nanostructuring – topography, chemistry and defined porosity, by ultrasonic and electrochemical treatments – to provide smart tissue scaffolds and lab-ob-chip systems. Active chemicals can be encapsulated into the metal surface (Small, 2012, 8, 820.3) to control spatially and temporary their release by stimuli. Formation of surface Layer-by-Layer (LbL) (Adv. Funct. Mater., 2009, 19, 2373.) coatings provides control of 4D surface behavior and relevant for lab-on-chip systems.

COLL 303

Silk macromolecules with amino acid-poly(ethylene glycol) grafts for controlling LbL encapsulation and aggregation of recombinant bacterial cells

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Cell encapsulation can provide enhanced mechanical, chemical, thermal, and radiation stability to the encapsulated cells, making it an attractive technique for biotechnology applications which require harsh conditions. The selection of polymers is constrained by the requirement for the polymer and polymer deposition conditions to be bio-compatible. Our work focuses on the usage of ionomers generated from modification of regenerated silk fibroin (SF) with a brush-grafting of several side chains, including poly-l-lysine (SF-PLL), poly-l-glutamic acid (SF-PGA), and poly(ethylene glycol) (PEG). By varying the grafting degree and the molecular weight of poly amino acids and PEG, we were able to assess the formation of cytocompatible and robust layer-by-layer (LbL) shells on bacterial cells. We observed that shells assembled with charged polycationic amino acids adversely effected the properties of microbial cells while promoting the formation of large cell aggregates. In contrast, hydrogen-bonded shells with high PEG grafting density were the most cytocompatible, while promoting formation of stable colloidal suspensions of individual cell encapsulates. The mechanical properties of these shells were assessed using force-volume measurements and development of a complex layered structure contact mechanics model. This approach allowed for a sophisticated understanding of the cell-shell interactions in vitro.

COLL 304

Hydrogen-bonded polymer nanocoatings as mediators of T cell immunity
Type 1 diabetes is an autoimmune-mediated disease resulting in the destruction of insulin-secreting pancreatic b-cells. Transplantation of insulin-producing islets is a viable treatment to restore euglycemia in Type 1 diabetics, however, the clinical application remains limited due to the use of toxic immunosuppressive therapies to prevent immune-mediated rejection. We present a nanothin polymer material with dual antioxidant and immunosuppressive properties capable of modulating both innate and adaptive immune responses crucial for transplantation outcome. Through the use of hollow microparticles (capsules) comprising of hydrogen-bonded multilayers of natural polyphenol (tannic acid) with poly(N-vinylpyrrolidone) (TA/PVPON) and with poly(N-vinylcaprolactam) (TA/PVCL), pro-inflammatory reactive oxygen and nitrogen species are efficiently dissipated and the production of IFN-γ and TNF-α pro-inflammatory cytokines are attenuated by cognate antigen-stimulated autoreactive CD4+ T cells. Our results provide evidence that TA-containing capsules are efficacious in immunomodulation and may provide physical transplant protection and prevent diabetogenic autoreactive T cell responses. Our results also suggest that transplantation of (PVPON/TA)- or (PVCL/TA)-coated islets may decrease the risk of xeno- and allograft rejection due to the attenuation of oxidative stress and pro-inflammatory cytokine synthesis, and ultimately, enable Type 1 diabetics a lifestyle independent of exogenous insulin administration.

COLL 305

Surface charge density in PEMUs and its influence on cell adhesion

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There is general agreement that cells grown on polyelectrolyte multilayers (PEMUs) better when the surface is negatively, as opposed to positively, charged. Cytotoxicity observed with positively-charged films is attributed to free polyelectrolyte chains disrupting the cell membrane. However, there are cases where cells grow regardless of the film surface charge. To understand this behavior 3T3 fibroblasts were cultured on a series of PEMUs, made from poly(diallyldimethylammonium), PDADMA, and poly(styrene sulfonate), PSS. The cells showed a variety of attachment modes, depending on the charge of the last layer and deposition conditions. Cells adhered poorly to all PSS-capped films, while PEMUs terminated with PDADMA were cytotoxic when built in 1.0M NaCl but cytophilic when built in 0.15M NaCl. This last result is contradictory, how can surfaces with the same chemistry be toxic and non-toxic? A group of "salt hybrid" films was designed to explore these findings. These films were built at one specific salt condition but capped at a different salt concentration keeping
the polymer concentration constant, e.g. PEMUs built in 0.15M NaCl but terminated with a layer of PSS in 1.0M NaCl. These hybrids should eliminate mechanical properties as a variable while comparing with the native film, leaving only film surface responsible for any changes in cell behavior. As expected, no significant differences in thickness, roughness or wetting were observed, however PDADMA-capped films lost their toxicity, and more surprisingly PEMUs built in 0.15M NaCl but terminated with a layer of PSS in 1.0M NaCl induced most cells to form floating spherical clusters after 48 hours of culture. When they were re-plated on control culture plastic, cells emerged with close to 100% viability. Differences between the various surfaces were probed in an effort to identify the mechanism responsible for this unusual behavior, which did not follow accepted correlations between substrate stiffness and cell adhesion between cluster-inducing PSS-capped multilayers and those that did not produce clusters. When the surface charge density was assayed with radiolabeled ions a strong increase of negative surface charge was revealed. Viewing the multilayer as a zwitterionic solid and comparing its surface charge density to that of a cell membrane yields similarities that suggest a mechanism for preventing protein attachment to the surface.

 COLL 306

Cancer cells/stromal cells co-culture on polyelectrolyte multilayer films: A template for studying cell-cell interaction in tumor progression

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We engineered patterned co-cultures of breast cancer cells and stromal cells on polyelectrolyte multilayer (PEM) films without the aid of adhesive proteins/ligands to study the role of cell-cell communication in tumor progression. A number of studies have explored engineering co-culture of tumor cells and stromal cells predominantly using conditioned media or transwell co-cultures, however these methods do not recreate the direct cell-cell contact prevalent in the tumor microenvironment. In our study, we used synthetic polymers, namely poly(diallyldimethylammoniumchloride) (PDAC) and sulfonated poly(styrene) (SPS) as the polycation and polyanion, respectively, to build the multilayers. We employed two developmentally distinct human breast cell lines for co-culture development and two different types of stromal cells, mammary epithelial cells (MCF10A) and mesenchymal stem cells (MSCs) to demonstrate the versatility of our platform. In this study, we capitalized upon this differential cell attachment and spreading of breast cancer cells on PDAC and SPS surfaces to make patterned co-cultures of breast cancer cells and stromal cells on the PEM surfaces. PDAC (or SPS) was patterned on the (PDAC/SPS)$_{10}$ surfaces by capillary force lithography, to obtain patterns of cancer cells and stromal cells. We further used the patterned co-culture system to study the effect of direct cell-cell contact on tumor biology. We demonstrated that the tumor cells in co-culture with MSCs proliferated and migrated more significantly compared to single culture of tumor cells. The results suggest that this technique may provide a useful tool for engineering tumor
microenvironment co-culture systems, that may more accurately capture tumor biology, and thus could be used to obtain valuable insights into tumor progression and perhaps even the pathogenesis of cancer.

**Step 1:**

(PDAC/PSS)$_{10.5}$

Poly(styrene sulfonate) (PSS)

Poly(diallyldimethylammoniumchloride)(PDAC)

- Layer-by-layer deposition
- PDMS Mold

**Step 2:**

Deposit polymer at inlet

- PDMS Mold

- Capillary action pulls polymer through channels

**Step 3:**

Allow solvent to evaporate

- PDMS Mold

**Step 4:**

Remove PDMS mold

- PDMS Mold

**Step 5:**

Seed first cell type

- Breast Cancer Cell

**Step 6:**

Seed second cell type

- Stromal cells

### COL 307

**Protein structures at device interfaces**
Functional protein and ligand structures at synthetic surfaces are needed in multiple contexts, including theragnostics, tissue engineering and other implants. We present our recent work on modifying surfaces for targeting nanoparticles onto cell surface receptors, as well as fundamental underlying property studies. The emphasis in this talk will be on multimodal methods to control protein structure at hydrophilic/hydrophobic/and amphipilic surfaces, and the tools to characterize the structures of proteins in situ. Examples will be drawn from devices to target functional proteins as well as pathogenic amyloid structures. We will report novel Raman spectroscopic and atomic force microscopy analytic approaches that give signatures with adequate molecular detail for modeling macromolecular structural change as it relates to interface change.

COLL 308

Characterization of protein and binding at model interfaces for optimization of activity

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The control of orientation and conformation of proteins at surfaces as well as the binding affinity is critical to maintain biological function in applications such as biosensing. In our recent work, we have probed the binding orientation, conformation, and affinity of proteins at model surfaces using techniques including surface plasmon resonance, atomic force microscopy, and ellipsometry. The use of model substrates to control the position of binding sites on the surface is achieved through AFM based patterning methods. These techniques have been applied to several protein systems including the F$_1$ ATP Synthase and the results suggest that further optimization of the ligand presentation at the surface will be required for optimal activity.

COLL 309

Self-assembly of polypeptides on metal surfaces in vacuum by soft-landing electrospray ion beam deposition

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Folding of proteins and peptides into one specific conformation is nature’s powerful and robust self-assembly route to molecular functionality. Encoded in the sequence of a polypeptide is the information about its folded structure, biochemical function as well as the folding mechanism. At surfaces the self-assembly of molecules is considered a
promising path to specific functionalization. The same set of binding motifs that generate a folded protein or peptide creates molecular networks of a vast variety on surfaces. Characterizing these structures typically requires atomic or submolecular level investigation by scanning tunneling microscopy (STM) and hence preparation on ultrapure, atomically defined substrates in ultrahigh vacuum.

Even though an impressive variety of molecular nanostructures and networks has been demonstrated using small synthetic molecules, so far polypeptides have not been utilized due to their thermal instability which inhibits thermal sublimation as deposition process. Using the short natural polypeptides Angiotensin and Bradykinin, here we show the formation of rational, highly ordered molecular nanostructures and extended molecular networks. We use soft landing electrospray ion beam deposition (ES-IBD) for the gentle deposition of the peptides onto the surface where we can observe their structure at amino acid spatial resolution by STM. We show that the polypeptide chains change their conformation to adopt to the surface and to other neighboring polypeptides and identify typical structural motives, similar to beta-turns or the separation of hydrophilic-hydrophobic residues in native protein structures. The adsorption geometry is analyzed with the help of molecular dynamics modelling of the adsorbed peptides.

This work shows that folding and self-assembly of peptides at surfaces is a novel route to the formation of molecular nanostructures, which bear the potential to act as tunable functional sites. To this end, the method of ES-IBD allows to rationally incorporate metal centers or choose relevant conformations via ion mobility selection.

STM micrograph of Bradykinin dimers on a Cu(100) surface formed by folding and self-assembly of two Bradykinin molecules.

COLL 310

Improving in vivo brain neurotransmitter sensors

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Molecular recognition is central to in vivo neurotransmitter sensing. We are developing and improving a number of different strategies focused on investigating serotonin transmission in the brains of behaving animals. Approaches include improving current methodologies such as increasing temporal dynamics in microdialysis and tackling problems associated with chemical selectivity in voltammetry. Advances in both of these approaches are yielding new information about serotonin signaling in the brain and encoding of emotionally salient information. Further, we are developing field-effect-transistor-based neurotransmitter sensors. The latter provide benefits in terms of spatial and temporal resolution, and sensitivity. Strategies for imparting molecular recognition via identification of high-affinity nucleic acid aptamers for small-molecule neurotransmitters are imparting the chemical selectivity needed for in vivo neurotransmitter measurements using FET-based sensors.

COLL 311

Force-based identification of single DNA bases with polymerase-tethered AFM tip

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The DNA sequence is a blueprint for life. To understand the role of each gene and to know the genetic variations of an individual would promise the preventive and personalized medicine. Single-molecule sequencing techniques have been developed to analyze DNAs of minimal sample amount with no requisite of amplification. Here, we report a new method to sequence single DNA molecules with high accuracy using AFM force spectroscopy. We immobilized a DNA polymerase on a dendron-coated AFM tip and four dNTPs on the separated areas of a glass slide. The polymerase was allowed to capture a target DNA, and four nucleotide spots were examined sequentially by force mapping. The DNA base located in the active site of polymerase could be determined by observing specific interaction force upon the examination of complementary nucleotide spot. The recognized base could be incorporated in solution dissolving the corresponding dNTP, and two steps, the recognition and incorporation, were repeated to read the sequence. Additionally, DNAP activity to incorporate the surface-immobilized dGTP was investigated under various applied forces.
Dynamic covalent control of nanoparticle properties and self-assembly

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Despite tremendous advances in nanoparticle (NP) synthesis and characterization, the range of strategies for controlling and interrogating NP surface functionality remains somewhat narrow. The preeminent oligonucleotide-based approaches only operate within tightly defined conditions, and offer limited scope for customization. Postsynthetic covalent modification of NP-bound monolayers is an attractive alternative, but traditionally this strategy has relied on kinetically controlled reactions, which produce statistical mixtures of products and only offer one-shot opportunities for modification. We have developed the concept of dynamic covalent nanoparticle (DCNP) building blocks as a ‘best-of-both-worlds’ strategy that combines the error-correcting and stimuli-responsive features of equilibrium processes with the stability and structural diversity of nonbiomolecular covalent chemistry.1 Here we will discuss the development of the DCNP concept, exemplified on monolayer-stabilized AuNPs, including: the effects of surface confinement on dynamic covalent reactivity; the reversible modulation of NP physicochemical properties under mild conditions; and reconfigurable NP self-assembly with molecular control over superstructure morphology. Dynamic covalent nanoparticle building blocks can provide a universal strategy for the manipulation of NP-bound molecular functionality. Such capabilities will be crucial for virtually any application that seeks to exploit the unique properties observed in this region of chemical space.

This work describes a rational strategy to obtain self-assembled two-dimensional (2D) nanocrystals with definite and uniform thickness from a series of molecular Janus particles based on molecular nanoparticles (MNPs). MNPs are 3D framework with rigid shapes. Three different types of MNPs based on derivatives of polyhedral oligomeric silsesquioxane (POSS), [60]fullerene (C60), and Lindqvist type polyoxometalate (POM) are used as building blocks to construct these amphiphilic molecular Janus particles by covalently connecting hydrophobic crystalline BPOSS with a charged hydrophilic MNP. The formation of 2D nanocrystals with an exact thickness of double layers of molecules is driven by directional crystallization of the BPOSS MNP and controlled by various factors such as solvent polarity, number of counterions, and sizes of the MNPs. Strong solvating interactions of the ionic MNPs in polar solvents (e.g., acetonitrile and dimethylformamide) are crucial to provide repulsive interactions between the charged outlying ionic MNPs and suppress further aggregation along the layer normal direction. The number of counterions per molecule plays a major role in determining the self-assembled morphologies. Size matching of the hydrophobic and ionic MNPs is another critical factor in the formation of 2D nanocrystals. Self-assembly of rationally designed...
molecular Janus particles provides a unique “bottom-up” strategy to engineer 2D nanostructures.

Reference:
sphere, which severely limits their characterization using Small Angle X-ray Scattering (SAXS). These elastic scattering formulae may be derived for polyhedral particles by taking advantage of Fourier transform and inversion symmetry. To do so efficiently, we discuss methods to break a particle into the least congruent set of pieces, or subunits. The effects of anisotropic form factor scattering are examined. Further, advances in nanoparticle synthesis and functionalization have allowed for corresponding advances in the assembly colloidal nanoparticle superlattices, resulting in a myriad of crystal symmetries using spherical as well as polyhedral particle building blocks. Understanding the forces that govern particle assembly requires knowledge of the crystal (superlattice) symmetry and interaction potential, which may be inferred from the lattice parameters. This task becomes challenging as these potentials often vary with the surrounding environment, such as pH, ionic strength, depletent concentration, and particle concentration. Thus, characterization tools such as SAXS that allow one to examine superlattice assembly in real sample environments and in real time become increasingly important. We will discuss the theoretical framework necessary to extend powder diffraction theory to the small angle regime, which will allow researchers to easily calculate the diffraction of nanoparticle superlattices composed of spherical and polyhedral building blocks. These calculated scattering spectra will be compared to a variety of experimental systems, including the assembly of cube, rhombic dodecahedra and octahedra nanoparticle building blocks using depletion-based assembly approaches. We further discuss the possibility of using SAXS for the characterization of exotic superlattice phases, such as the rotator crystal, which possess long-range positional order but where the particles are able to rotate randomly about their lattice points.

COLL 315

2D and 3D clustering via self-assembly depending on chemical and geometrical anisotropy of Janus microcylinders

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For the last decades, self-assembly at various scales have been highly studied as an alternative manufacturing process for formation of various functional materials. There are quite a number of reports related to understanding of various parameters for controlling of self-assembly at molecular and supramolecular scale such as pH, light, salt as external parameters or intermolecular interaction including van der waals, H-bonding, electrostatic interaction, and hydrophobic interaction. However, these molecular self-assembly hardly provide large-scale assembled structures at micro and millimeters.

Alternatively, particle building blocks including colloids, micro and millimeter particles are promising for generation of micro and mesoscale assembled structures, but there
are a few studies about the various parameters for controlling of self-assembly using microparticles. So, it is strongly required to study self-assembly with various parameters to extend formation of self-assembled structures with minimization of defect and reproducibility.

This study presents self-assembly of Janus microclinyders with controlled chemical and geometrical anisotropy. Micromodling integrated with initiated vapor deposition (iCVD) produce momodispers flat-top or convex-top Janus microcylinders with controlled hydrophobicity and hydrophilicity. The results shows 2D and 3D clustering of Janus cylinders driven by hydrophobic interaction and geometry. The number of Janus cylinders comprising 2D or 3D clusters are highly depends on the hydrophobicity and hydrophilicity of the Janus cylinders.

We envision that the experimental results studied including design of Janus cylinders for self-assembly are potentially extend a novel desing route for generation of ordered structures in microscale.

COLL 316

Fabrication of 3D structured particles by wetting fluids with tunable mold swelling and capillarity on micromolds

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Polymeric colloidal particles with 3D geometry play an important role in drug-delivery materials, building blocks for self-assembly, multiplexed assays. Especially, in drug-delivery applications, non-spherical particles with different surface areas can provide tunable releasing kinetics through the controlled degradation of polymeric networks. However, some techniques for preparing specific 3D structured particles still faces challenges with regard to scalability, simplicity, and controllability.

Herein, we present a strategy for fabricating the 3D structured microparticles on micromolds utilizing some merits of tunable mold swelling and capillarity of wetting fluids. We modulate the spatial deformation of a photo-curable solution loaded in micromolds using wetting fluids with distinct properties to give them complex shapes and sequentially polymerize the deformed polymeric fluids into 3D structured particles. The 3D structured particles show high uniformity with controlled geometry from identical 2D micromolds via simply tuning the wetting fluids. Also, we generate complex microparticles with distinct compartments by combining sequences of discrete wetting fluids with different mold swelling and capillarity. We envision that this approach for producing 3D structured particles from easily designed simple micromolds could contribute to new colloidal science and materials.
3D structured and multicompartmental particles produced by wetting fluids with mold swelling and capillarity on micromolds.

COLL 317

**Dynamic self-assembly of nanoparticles: Achieving switchable metamaterials**

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Obtaining ordered aggregates of nanoparticle is a formidable challenge in materials chemistry. Such materials exhibit unique physicochemical characteristic resulting from distant-dependent collective interactions of individual building blocks. Unfortunately, most of the available assembly methods result in **static self-assembly**, that is once formed, aggregates maintain their structure. To achieve active tunability of aggregate
features it is necessary to develop **dynamic self-assembly** strategies, which is the focus of our work (e.g. Lewandowski W, et al. *Nat Commun.* 2015, 6, 6590).

Here, we show that by using liquid-crystalline molecules grafted onto the surface of nanoparticles we are able to prepare nanoparticle superstructures that exhibit thermo- and photoresponsive behaviour, with both structural and functional tunability. These long-range ordered structures can be reversibly switched between lamellar and isotropic phases (Figure 1) which is accompanied by the change of plasmonic properties of the assembly. Most interestingly, for Ag nanocrystal-based system we have theoretically predicted **tunable metamaterial** (epsilon-near-zero in the visible) behavior. We will also discuss our latest achievements in preparing structures showing long-to-long range order transition and faster kinetics of rearrangement. These structures are based on different kinds of nanoparticles. Direct correlation of optical structure-property relationship was established.

**COLL 318**

**Sol-gel method: An advanced technique to obtain a 3D superstructure of metal-semiconductor hybrid nanoparticles**

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The groundwork of nanoscience is based on the principle of colloidal materials that exhibit novel physical properties compared to their bulk counterparts. Surface characteristics of these colloidal particles have direct influence over their physical properties that can be attained only by modifying parameters such as size, shape, and geometry. Metal and semiconductor hybrid nanostructures (HNSs) has attracted much attention due to the potential of coupling high absorption cross sections and size tunable optical properties of semiconductor nanoparticles (NPs) with the localized surface plasmon resonance (LSPR) of metal NPs. Sol-gel technique via oxidative removal of surface ligands, is one of the powerful technique that can be employed to obtain three dimensionally connected porous super structures. The morphology of the HNSs has crucial importance, as the optical property will largely depends on the shape
and physical distance between the NPs. In 3D gel framework the metal and semiconductor NPs will be in close proximity that can enhance the overlapping of their electronic states, giving rise to new optical characteristics of the HNSs. This synergistic effect of the metal-semiconductors can be use to tune the optical property of the aerogel structures that can be useful in various optoelectronics, biomedical imaging, solar cells, and photocatalytic applications. Characterization of this metal-semiconductor aerogels were carried by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, surface area and porosimetry, UV-visible, photoluminescence, and time resolved photoluminescence analysis. The result of morphology, surface area and optoelectronic properties of metal-semiconductor gel network will be discussed.

**COLL 319**

**Charge induced adsorption of string-like particles for omnidirectionally transparent superhydrophobic surface**

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Nanoparticle coatings have attracted significant interest during recent years due to compatibility with scalable and inexpensive coating techniques and variety of substrates. The formed nanostructures is essentially a film-like assembly of
nanoparticles with morphology and properties determined by their nanoparticle building blocks and, more importantly, how these particles are assembled. Charge induced adsorption of nanoparticles provides a unique approach to uniformly deposit an ultra-thin layer (10’s or 100’s nm thick) of particles, majorly attributed to its self-limiting nature. As the surface coverage reaching saturation (i.e., a dense layer of particles), further adsorption of particles becomes prohibited due to the electrostatic repulsion from the already adsorbed particles. So far, nanoparticle coating research has focused on spherical nanoparticles to understand the coating mechanism and create coatings for applications, e.g. anti-reflectivity, self-cleaning, and anti-fogging. Few have paid attention to anisotropic nanoparticles. In our study, negatively charged anisotropic silica nanoparticles with string-like morphology were adsorbed onto a positively charged surface in an aqueous environment. The coating morphologies at different coating time were investigated via both AFM and SEM. Self-limiting kinetics of adsorption was observed. At pH 6, the average coating thickness was saturated at ~50 nm, and the coating coverage was ~45%. Interestingly, the surface roughness generated during the adsorption of string-like particles was found much higher compared to those from spherical particles prepared at similar conditions. We attributed the enhanced roughness to the distinctive adsorption mechanism associated to the anisotropic nanoparticles, where the particles could interact with the surface upon different orientations (e.g. at the sides or the ends, Fig. 1). As a result, upon drying, the string-like particles could re-orient and stack against each other to build up surface roughness more effectively. After hydrophobilizing the surface, we demonstrated that the coatings can offer both superhydrophobicity (a water contact angle ~ 170°, and contact angle hysteresis < 2°) and meanwhile an optimized omnidirectional transparency.

![Figure 1. Schematics showing the formation of the coating by charge-induced adsorption of string-like particles](image.jpg)

**COLL 320**

Ultra-large-area SERS-active monolayers fabricated by assembly of anisotropic Au/Ag core/shell nanoparticles
Large-area close-packed monolayers of one-dimensional nanoparticles, such as spheres, can be easily fabricated by interfacial self-assembly method on the surface of water. However, monolayers of anisotropic gold nanoparticles, especially synthesized in the water phase containing hydrophilic surfactant CTAB, are very challenging. This report describes a facile and low-cost method to fabricate ultra-large-area monolayers of gold nanorods based Au/Ag core/shell nanoparticles by using the Langmuir-Blodgett technique. Firstly, CTAB/CTAC coated Au/Ag core/shell nanoparticles with different shapes are transferred from water-phase to oil-phase by poly(vinylpyrrolidone) (PVP) and dodecanethiol functionalization without any aggregation. These nanoparticles can be well dispersed in a ternary solvent mixture, and then spread over the water surface. Due to the difference in solvent volatility and partial coverage of the home-made trough, the nanoparticles can be drove to move by the evaporating flux toward the front of the uncovered interface, leading the formation of a dense monolayer. The monolayers are easily transferred onto different substrates, silicon wafer, glass slide and TEM grid. The largest obtained area of a continuous monolayer is ~2 cm². Large numbers of hot spots in the monolayers can be produced by the close-packed arrangement in the inter-particle regions (end-to-end and edge-to-edge) and the gap region (core-to-shell), providing strong surface-enhanced Raman scattering (SERS) signals. This method can also be applied to other nanostructures for film fabrication, which are expected to serve as excellent SERS substrates with high enhancement factors.
Sol-gel method for the assembly of noble metal nanoparticles into metallic aerogels

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The novel physical properties observed in nanostructured solids are attributed to the dramatic changes in the electronic structure as well as the large surface area, which make them more chemically reactive than corresponding macroscopic solids. These unique properties have led to the development of synthetic methods that permit exquisite control over materials size, shape, and polydispersity in the nanometer length scale. The aerogels derived from metal and semiconductors NPs represent an emerging class of superstructures with enormous potential in catalytic, optoelectronic, photonic, and sensing technologies. Significant efforts have already been devoted to the assembly of metal nanoparticles utilizing organic ligands, polymers, biomolecules, and templating strategies. The ability to form nanoparticles superstructures by direct cross-linking of metal, semiconductor, and metal/semiconductor hybrid NPs has recently been realized through a modified sol-gel synthetic technique. Our group has reported the sol-gel method utilizing for the assembly of Ag nanoshells (NSs) into high surface area metallic Ag aerogels. In this regard, we have expanded this technique to prepare novel materials such as Ag, Au, and Pt ternary alloy nanoparticles and resultant aerogels. These materials will be applied to be the catalysts of direct methanol/ethanol fuel cells, and hopefully they will overcome so many problems such as the catalyst poisoning, efficiency, substrate and cost.

Porous conducting superstructures of metal colloids: Noble metal aerogels

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The assembly of nanoparticles into functional superstructures is an important challenge that needs to be addressed for the generation of nanoparticle-based devices. Sol-gel method has proved useful for the direct-assembly of metal, semiconductor, and their hybrid nanoparticle systems into high surface area, highly conducting mesoporous superstructures (aerogels). In contrast to traditional metal oxide sol-gel synthesis, where gelation is achieved through hydrolysis and condensation of molecular precursors, the gel formation in nanoparticle-based systems is induced through oxidative removal of surface functionalities of colloidal nanoparticles. In this study, the application of the later strategy for the self-assembly of binary and ternary noble metal colloids into conducting metal nanoparticle superstructures is described in the context of their use in electrocatalysis. The effect of synthetic parameters and physical characteristics of the
nanosized objects on morphology, surface area and porosity, electrical and thermal conductivity, optical transparency and opacity of metal nanoparticle superstructures will be discussed.

** COLL 323**

**Conformation, effective interactions, and assembly of polymer-coated nanoparticles at liquid interfaces**

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Adsorption at liquid interfaces is a powerful way to drive the self-assembly of nanoparticles because the adsorbed objects can still move and rearrange to form various 2-dimensional structures. Obtaining high coverages and relatively fast self-assembly requires good control of the effective interactions and of the emerging dynamics of the nanoparticles at the interface. We have investigated the deformation of the polymer shell and effective interactions of polymer-coated nanoparticles adsorbed at a model liquid–liquid interface via molecular dynamics simulations. Starting from these results we have developed a numerical approach for the assembly of densely packed particle-laden interfaces, which accounts for the irreversible nature of the adsorption process. Inspired by a series of experiments on core-shell nanoparticles at oil-water and air-water interfaces, we follow the adsorption kinetics and elucidate its interplay with the particle dynamics at the interface. Our numerical studies show that, in presence of soft repulsive interactions, the adsorption may be slowed down by the crowding of the particles at the interface and that the adsorption kinetics and/or the size polydispersity can be used to tune the degree of ordering and the amount of defects at the interface.

** COLL 324**

**Gold nanoshells on soft structures: Process parameters effect**

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Gold nanostructures have attracted interest in many fields due to their surface plasmon resonance (SPR) properties. When gold nanostructures are exposed to light, depends on the size and shape, they can absorb light in different wavelengths which can be used for sensing and generating heat. Among gold nanostructures, gold nanoshells- due to their Near Infra-Red (NIR) absorption wavelength- have attracted interest in biomedical applications. Another advantage of NIR heating system is localized heating which allows treatment without harmful effects on healthy tissues. Combination of gold nanoshells with soft templates can be used for loading and controlled release of bioactive materials.
Liposomes are soft biocompatible templates that can be used for this purpose. Advantage of this substrate compared to solid substrates includes higher drug loading efficiency, loading different types of drugs, easier preparation, .... There are some studies out that used liposome as a template to create gold-shell structures but there is no study about the effect of different process parameters. In this study, different types of nanoshells are created and the effects of process parameters on the structure and properties will be investigated. According to the results, the pH of gold chloride solution is one of the most important factors in this process.

COLL 325

Star-polymer and colloid mixtures: Glassy states and arrested phase separation

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We investigate the effects of small, hard colloidal particles on star-polymer glasses by employing a recently introduced, coarse-grained picture of the binary mixture, and compare the theoretical predictions with dynamic light scattering and rheological measurements. Depending on both the star-to-colloid size ratio and the functionality (number of arms) of the stars, the addition of hard colloids can yield either melting of the glass or the emergence of two distinct glassy states. These findings are explained by depletion of the colloids adjacent to the stars, which leads to an arrested phase separation when the star glass line meets the demixing binodal. The agreement between experiment and theory suggests the generic nature of our results and opens the route for designing soft-hard colloidal composites with tunable rheology.

COLL 326

Motion of a nanoparticle in an unentangled polymer melt - passive and active microrheology

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Microrheology is based on monitoring the thermal or stimulated motion of suspended micro- or nanoscopic particles, from which the rheological properties of the surrounding material can be calculated. The results shown here are based on a molecular dynamics simulation study on passive and active microrheology of an unentangled polymer melt.
For this a simple polymer model similar to the bead-spring model of Kremer and Grest was used. In the simulations parameters like the sizes of the nanoparticle and the simulation box, the length of the polymer chains, the interaction between nanoparticle and polymers and temperature can be varied easily and hence their influence on the microrheological results can be investigated.

The outcome is, that at high temperatures and not too strong interaction between nanoparticle and monomers, there is a very good agreement between microrheological moduli and reference moduli, which are obtained from stress tensor calculations. At low temperatures, only local properties can be measured, because strong collective motions and a layering in structure and dynamics occur. For too strong interactions, hydrodynamic effects are no longer negligible and an improvement of the underlying equations is required.

To go also in the direction of nonlinear properties, different examples of active microrheology were studied. On the one hand, these are forced oscillations of the nanoparticle, adapted from oscillating optical tweezer experiments, which lead at low frequencies to the same results as the passive microrheology. Other examples are pulling the nanoparticle with a constant force or using an oscillator composed of two nanoparticles, that performs damped oscillations and for which there is no experimental analogy (yet).

**COLL 327**

**Floating superhydrophobic assemblies**

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Liquid marbles, liquid droplets coated by PTFE powder, at the water/air interface have been studied. An object, which floats at the water/air interface, causes a deformation of the interface. When two floating objects reach each others vicinity, to minimize the energy caused by the overlap of the deformations, the objects move towards or away from one another. Capillary forces cause these behaviors. In this work, we focus on the geometric effect of the water/air deformation on the assembling behavior. The reasons to choose liquid marbles as the objects to study are: 1) they remain at the interface, which is a prerequisite for capillary interaction; 2) the surface of a liquid marble is superhydrophobic, which helps to isolate the effect of the geometry of the water/air deformation from other parameters on the assembly; 3) the deformation of water/air interface can be easily changed just by varying the volume and density of the solution used to prepared the liquid marble. Dynamics of liquid marbles, when they assembled, were recorded and analyzed. The data were used to quantify the interactions. It was found that liquid marbles with different volumes assemble at different rates. To further study the effects of the geometry of the water/air deformation, surfaces with different curvature or surface chemistry were used to control the assembly of liquid marbles.
Structure and dynamics in polymer melts mixed with compact stars

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A molecular dynamics simulation study is presented for entangled melts mixed with particles of the order of the tube diameter or above. The choice of compact stars represents a model system of nanocomposites without polymer-particle adsorption. We present a system where the particles remain well dispersed over the whole concentration range and the stars are sufficiently compact that the pure system is jammed. For these particles in the order of the tube diameter, we observe a weak compression of the matrix chains with increasing volume fraction of stars. Short (unentangled) matrix chains get slowed down by adding particles to the system. When the matrix chains become significantly longer than the entanglement length, this trend is inverted and the matrix chains become faster because the particles dilute the entanglement network. The center-of-mass (CM) dynamics exhibits regimes of anomalous diffusion in accordance with viscoelastic hydrodynamic interactions (VHI) [J. Farago et al. PRL 107, 178301 (2011); PRE 85, 051807 (2012)].

At low and intermediate star-particles concentration, the particles themselves vary little in mobility, only at high concentration (above percolation), they become slowed down because of colloidal packing. As a result, the viscosity as a measure of the collective mobility drops when adding few particles to the melt because of disentanglement, and at high particle volume fraction the viscosity increases again because of colloidal caging.

Preliminary studies with particles larger than the tube diameter show that the stabilization of the mixture with purely entropic interactions is very delicate and disentanglement-effects are reduced.
Effects of defects and hydroxyl groups on adsorption and photoluminescence of zinc oxide

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Methanethiol and sulfur dioxide adsorption on single crystal zinc oxide surfaces and nanoscale powders has been investigated using X-ray photoelectron spectroscopy (XPS) and in-situ ultrahigh vacuum (UHV) Raman spectroscopy. Photoluminescence (PL) measurements have also been performed in UHV, and the role played by defects has been investigated by comparing the adsorption and PL spectra with and without energetic argon ion bombardment prior to gas exposure, which is known to create oxygen vacancy defects. The effect of coadsorbed hydroxyl groups has also been investigated by adsorbing water prior to methanethiol and SO$_2$ exposure. In the case of SO$_2$ exposure, sulfite is found form on ZnO(0001) and ZnO nanopowder surfaces. Strong S-Zn bond formation occurs for methanethiol adsorption, and the adsorbate is stable to temperatures of ca. 150°C. Both adsorbates dramatically affect the PL spectra. Changes in the electronic structure of ZnO(0001) due to sputtering, hydroxyl groups, and adsorption have been studied with ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopies, which probe the energies of the filled and empty electronic states of the surface, respectively. The experimental results are compared to DFT calculations on ZnO clusters.

COLL 330

AP-XPS and HERFD XAS as complementary operando probes in electrocatalysis

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A major challenge to the development of a renewable energy infrastructure is the mismatch between an abundant energy supply that is generated predominantly as electricity, and demand, especially in road transportation and aviation, that requires a portable energy source with high power and energy density that cannot be sufficiently met with electricity storage in batteries. This gap could be bridged with electrochemical conversion between electricity and fuels with high energy density. New catalyst materials will be needed to drive complex electrochemical conversions with multiple electron transfers at low temperatures with sufficient turnover and high product selectivity. The design of such new materials can be accelerated if we gain fundamental understanding of the electronic structure of the catalyst and the chemical bonding of reaction intermediates during operation. We have developed two complementary approaches for operando x-ray probing.
Operando hard x-ray absorption spectroscopy (XAS) probes the structure of the catalyst under reaction conditions. By using XAS in the high energy resolution fluorescence detection (HERFD) mode, we can obtain spectra with reduced effective lifetime broadening and thus much more detailed electronic structure information than conventional XANES. This technique, combined with computational modeling of the oxygen evolution reaction (OER), recently allowed us to identify the most active sites for OER in mixed Fe/Ni oxyhydroxides. While HERFD XAS is inherently bulk-sensitive and most suitable for the investigation of structure-activity relationships, we also achieved high surface sensitivity using well-defined monolayer model catalysts for the oxygen reduction reaction (ORR) in fuel cells where we demonstrated sensitivity to chemisorbed species.

In a highly complementary manner, we can access directly the core levels (e.g. C/N/O 1s) of chemisorbed species using soft x-ray photoelectron spectroscopy under ambient pressure (up to 100 torr). We have developed a membrane-electrode assembly in which chemisorbed species at operating electrocatalyst surfaces can be detected with XPS. We have successfully applied this technique to follow electronic structure changes at the surface of a MoS$_2$ catalyst for the hydrogen evolution reaction (HER), IrO$_2$ during OER and to distinguish different oxygen-containing species (H$_2$O, OH·H$_2$O, OH·O, O) at a Pt catalyst during ORR.

**COLL 331**

**In operando tracking of surface electrochemical redox activity in solid oxide electrochemical cells using near infrared radiation imaging**

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Near infrared (NIR) radiation imaging is used in conjunction with near ambient pressure X-ray photoelectron spectroscopy (APXPS) to study chemical and electrochemical redox processes on a ceria-based solid oxide electrochemical cell (SOC). Control experiments in which the SOC is exposed to either a reducing or oxidizing atmosphere (H$_2$ and H$_2$O, respectively) show that APXPS ceria redox state analyses correlate strongly with NIR imaging data in which ceria redox states are tracked by monitoring changes in NIR radiation emission. Electrochemical water electrolysis tests conducted in realistic operating conditions on a standard SOC show that NIR imaging can spatially resolve the electrochemically active regions that are associated with an accumulation of reduced ceria. These data correlate strongly with APXPS measurements, simultaneously validating the ability to use the near ambient conditions and single-sided cell set-up required by APXPS experiments and the ability to elucidate mechanistic details on an operating SOC using an inexpensive, accessible NIR imaging technique.
COLL 332

Vibrational sum frequency generation spectroscopy for probing the triple junction in heterogeneous catalysis

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This talk presents an overview of several papers the Geiger group has been publishing on vibrational sum frequency generation spectroscopic studies aimed at elucidating molecular views of heterogeneous catalytic processes. A specific example is provided with binary (hexanol in hexane) mixtures over aluminum oxide surfaces in the presence and absence of 2-nm Pd particles, and the hexanoic acid overoxidation product. Special attention is given to deuteration schemes for probing the solute/solvent/catalyst triple junction.

COLL 333

In operando studies of CuOx and MoOx model surfaces for application as chemical warfare agent destruction catalysts

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Filtration systems for absorption and decomposition of chemical warfare agents (CWAs) are the first line of defense against exposure to these toxic compounds. Composite materials (such as ASZM-TEDA) commonly used in filtration systems consist of high-
surface-area carbon supports impregnated with various metals and metal oxides. Despite decades of work to develop highly effective and versatile filtration materials with long-term usability, little is known about the mechanisms of CWA adsorption and degradation by material surfaces and catalyst deactivation and poisoning, in part due to the challenges involved with spectroscopic characterization of catalyst surfaces under operating conditions. Enabling the rational design of more advanced filtration and decomposition materials for broad-spectrum protection against CWAs and other toxic industrial compounds requires a sophisticated understanding of the chemical mechanisms behind CWA sorption and degradation on the molecular scale.

We will present the surface spectroscopic study of model CuO\textsubscript{x} and MoO\textsubscript{x} surfaces for catalytic decomposition of dimethyldimethylphosphonate (DMMP), a CWA simulant. Ambient-pressure XPS and NEXAFS enable examination of these surfaces during DMMP adsorption and reaction. Initial experiments indicate that adsorption of DMMP on these surfaces is observed at pressures as low as 1 × 10^{-7} Torr. On a Cu(111) single crystal and CuO\textsubscript{x}, decomposition of adsorbed DMMP occurs at this pressure and higher (60 mTorr). In contrast, decomposition on MoO\textsubscript{2} and MoO\textsubscript{3} surfaces only occurs upon heating above 100 °C. Possible mechanisms of DMMP degradation over these materials will also be discussed.

**COLL 334**

**In-operando characterization of the structural dynamics of supported heterogeneous catalysts during transformations of C-C and C-H bonds**

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It is now well appreciated that supported metal catalysts exhibit complex electronic and atomic structural properties, ones varying sensitively with the operating environments found in the *in-operando* environments of active processes. These structural and dynamical influences can be especially pronounced in important supported catalysts systems due to the impacts that arise as a consequence of finite metal particle sizes, localized perturbations due to metal-support interactions, and most importantly the strongly condition-dependent attributes of metal-adsorbate bonding. In this talk I will describe the experimental investigation of these factors, as well as the elucidation of the impacts they have on mechanism, within an exemplary class of catalytic reaction, olefin hydrogenation carried out over supported Pt-group metal catalyst. The underlying elementary reactions—processes that activate dihydrogen and, as will be shown, effect complex transformations of C-H, C-C, M-H, and M-C bonding *in operando*—significantly reshape the electronic and atomic structures of supported nanoscale Pt and Pd clusters in metal specific ways that further illustrate new features that reside within the rate-structure-property correlations of this exemplary class of reaction. In this talk I will discuss methods suitable for characterizing such features—highlighting new and emerging capacities for studying functional catalysts. I will discuss recent collaborative studies that have revealed dynamical features that underpin both condition responsive
bond-strains and perturbations of electronic structure in supported heterogeneous catalysts, and the nature of complex metal-support and metal-adsorbate mediated transformations of composition and bonding in working catalysts. The results extend insights into the structural dynamics manifested in these systems that harbor significant import for understandings of both their properties and mechanisms of action.

COLL 335

Monitoring catalytic surface phenomena under reaction conditions and establishing structure-activity/selectivity relationships

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It has now become possible to simultaneously monitor catalytic active sites (molecular and electronic structures), surface reaction intermediates and reaction products (kinetics) under relevant reaction conditions in real-time (operando spectroscopy methodology). Such fundamental information makes it possible to establish molecular/electronic structure – activity/selectivity relationships for catalytic systems and to molecularly engineer advanced catalytic materials for specific targeted applications. In recent years, this new approach has been applied by the Operando Molecular Spectroscopy & Catalysis Laboratory at Lehigh University to several catalytic reaction systems and recent research examples will be presented (olefin metathesis, ethylene polymerization, water-gas shift, methane activation to liquid hydrocarbons, biomass pyrolysis, etc.).

COLL 336

Elevated inhibition effect of self-assembled nanohydrogel of curcumin-hyaluronic acid conjugates on amyloid β-protein aggregation and cytotoxicity

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Aggregation of amyloid β-protein (Aβ) is a major pathological hallmark of Alzheimer’s disease. Curcumin has been recognized as an inhibitor of Aβ aggregation, but its low water solubility and bioavailability limits its clinical applications. In this work, we conjugated curcumin to hyaluronic acid and drastically improved its solubility. We found that the conjugates could self-assemble into nanosized hydrogels that inhibited Aβ fibrillogenesis and mitigated the amyloid cytotoxicity more efficiently than free curcumin. More importantly, we found that there was an optimal curcumin substitution degree, at which the hydrogel exhibited the strongest inhibitory effect. Based on these findings, a mechanistic model was proposed. It suggested that besides the inhibitory effect of the conjugated curcumin, HA provided two synergistic inhibitory functions. The first was the
counteraction of the hydrophobic binding between Aβ and the conjugated curcumin against the electrostatic repulsion between the like-charged Aβ and HA. The two opposite forces could slow down the aggregation and/or leading to off-pathway aggregations. The second was an isolation effect of the hydrogel network, which hindered the interactions between Aβ molecules. This work offered new insights into the development of more potent inhibitors for Aβ fibrillogenesis and cytotoxicity.

**COLL 337**

**Intravenously administered nanoparticles halt bleeding and protect the central nervous system after trauma**

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Traumatic injury is the leading cause of death for both men and women between the ages of 5 and 44 worldwide, and blood loss is the primary cause of death at acute time points post injury in both civilian and battlefield traumas. Immediate intervention is critical to minimize mortality associated with severe trauma, and yet there are no methods to cannot address internal injuries in the field. Hemorrhaging is also the first step in the injury cascade in the central nervous system (CNS). In both spinal cord and traumatic brain injuries, the first observable phenomena, regardless of mechanism of insult, is hemorrhaging. If one can stop the bleeding, can one preserve tissue and improve outcomes? The primary mechanical insult is very often a small part of the injury. The secondary injury processes that occur over hours, days, and weeks following injury lead to progression and the poor functional outcomes. Stopping those secondary injury processes would mean preservation of greater amounts of tissue. Preservation of tissue means better functional outcomes.

We have developed hemostatic nanoparticles are effective at stopping bleeding and improving survival over both the short and long term in multiple models of trauma including liver injuries as well as CNS injuries. These particles are exceptionally simple: PLGA-based nanospheres functionalized with PEG terminated with variants of the RGD motif. The particles lead to a reduction in bleeding which correlates with better neurological outcomes after injury as well as less neural degeneration. This effect is augmented when we leverage the particles as a drug delivery system and deliver a steroid, dexamethasone. Overall, these hemostatic nanoparticles offer a potential approach to stop bleeding, improve survival, and, potentially, limit CNS injuries.

**COLL 338**

**pH-Responsive intracellular degradable hydrogel cubes for cancer therapy**
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We report on a novel type of shaped hydrogel nano- and micro-particles which undergo rapid, and reversible volume changes in response to intracellular pH. The cubic hydrogels are produced as interconnected poly(methacrylic acid) (PMAA) network replicas of mesoporous manganese oxide templates by sequential infiltration of (PMAA) and poly(N-vinylpyrrolidone) (PVPON), followed by cross-linking of PMAA and template dissolution. The integrated advantages of the porous cubic sacrificial templates and responsive PMAA matrix enable synthesis of monodisperse and pH-sensitive hydrogel cubes in a rapid, facile, and reproducible manner. These cubic and spherical networks maintained their three-dimensional (3D) shapes in dry state and reversibly swelled up to 2-fold in response to pH variations maintaining their 3D shape. The swelling of the cubic and spherical hydrogel particles is controlled by the network structure which is regulated by PMAA molecular weight and crosslinker hydrophobicity. No cytotoxicity is found for the cubic and spherical hydrogels upon their interactions with human cancer cells for various time intervals. pH-triggered loading and release of doxorubicin to and from the hydrogels is shown and their anticancer effect is demonstrated. The doxorubicin-loaded cubic and spherical hydrogels decreased the cell viability by 90% after 48 h of cell incubation. We also found the effect of the hydrogel 3D shape on the cellular internalization for HeLa cells. The approach presented here provides a new platform of multi-functional particles with highly-controlled geometry, size, composition, and responsive properties to be potentially used in targeted drug delivery for cancer therapy.

COLL 339

Self-assembled nanoparticles containing cyclodextrins and their application in targeted drug delivery

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Cyclodextrins and cyclodextrin complexes self-assemble to form invisible nanoparticles with diameter of about 20 to 200 nm. Under certain conditions these nanoparticles can self-assemble further to form small microparticles with diameter of up to couple of μm. Cyclodextrin aggregation is guest induced and the size of the aggregates depends on the properties of both the guest and the cyclodextrin molecules. The degree of aggregation depends on the availability of the guest/cyclodextrin inclusion complexes in the aqueous media, increasing with increasing complexation efficiency. Most importantly, the aggregates are in dynamic equilibrium, free molecules with the individual complexes, individual complexes with small aggregates and small aggregates with larger aggregates (Figure). The discovery of drug/cyclodextrin complex aggregates has had profound influence on the pharmaceutical applications of cyclodextrins, not only on their usage as solubilizers and stabilizers of drugs but also on their usage as drug delivery carriers. In most cases cyclodextrins enhance drug delivery through biological
membranes by increasing drug permeation through the unstirred water layer (mucus) at the membrane exterior. Examples will be given of how cyclodextrin nanoparticles can enhance drug delivery from the skin surface into hair follicles, and how cyclodextrin nanoparticles and microparticles enhance drug delivery from the eye surface into both anterior and posterior segment of the eye, such as to the retina.

Self-assemble of drug/cyclodextrin complexes in aqueous solution

**COLL 340**

**Cancer vaccine using crosslinked CpG oligonucleotide/β-glucans nanoparticles**

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Cancer vaccine comprising cancer antigens and adjuvant is one of the new cancer treatments and can induce immune-responses to cancer cells specifically. CpG oligonucleotides (CpG-ODNs) are known to be a new adjuvant. CpG-ODN is recognized by toll like receptor 9 (TLR9) in endosome and induces immune-responses after it is taken up by antigen presenting cells (APCs). However, CpG-ODN is easy to be degraded by enzyme in biological fluids. To solve this issue, the development of carrier to deliver CpG-ODN into APCs has been studied.

We have studied a polysaccharide schizophyllan (SPG), a member of β-glucans, as a delivery carrier of oligonucleotides. SPG can form a complex with oligonucleotides¹ and prevents degradation by biological enzymes. We have reported that the complex comprising of SPG and CpG-ODN (CpG-ODN/SPG) can induce high immune responses². (Figure.a) According to recent studies, there is a particular range in size for molecular recognition or cellular uptake. Therefore the preparation of larger or smaller particles with CpG-ODN/SPG would enhance the present immune-responses.

In this study, we prepared a large particle by use of CpG portions as a crosslinking point. (Figure.b) We mixed CpG-ODN/SPG with complementary CpG (cCpG)-ODN/SPG...
at the same molar ratio and examined the reaction mixture with gel electrophoresis and dynamic light scattering. (Figure.c) From the migration pattern and size distribution of the reaction mixture, we observed the larger particles than CpG-ODN/SPG, resulting in the large particles (crosslinked CpG-ODN/SPG). The splenocytes treated with crosslinked CpG-ODN/SPG produced more cytokines than those treated with CpG-ODN/SPG\(^3\) (Figure.d). These results suggest that the crosslinked CpG-ODN/SPG can be used as a potent adjuvant for cancer vaccination and virus. (Figure.e)


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**Figure.** a) The structure of polysaccharide called schizophyllan (SPG), b) Crosslink nanogel was design by using complementally CpG. c) particle size by agarosegel, d) IL-6 response, e)CTL activation

**COLL 341**

Silver nanoparticle-embedded polymersome nanocarriers for the treatment of antibiotic-resistant infections
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The rapidly diminishing number of effective antibiotics that can be used to treat infectious diseases and associated complications in a physician’s arsenal is having a drastic impact on human health today. This study explored the development and optimization of a polymersome nanocarrier formed from a biodegradable diblock copolymer to overcome bacterial antibiotic resistance. Here, polymersomes were synthesized containing silver nanoparticles embedded in the hydrophobic compartment, and ampicillin in the hydrophilic compartment. Results showed for the first time that these silver nanoparticle-embedded polymersomes (AgPs) inhibited the growth of \textit{Escherichia coli} transformed with a gene for ampicillin resistance (bla) in a dose-dependent fashion. Free ampicillin, AgPs without ampicillin, and ampicillin polymersomes without silver nanoparticles had no effect on bacterial growth. The relationship between the silver nanoparticles and ampicillin was determined to be synergistic and produced complete growth inhibition at a silver-to-ampicillin ratio of 1 : 0.64. In this manner, this study introduces a novel nanomaterial that can effectively treat problematic, antibiotic-resistant infections in an improved capacity which should be further examined for a wide range of medical applications.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The proliferation of ampicillin-resistant \textit{E. coli} was measured over 24 hours in the...}
\end{figure}
presence of (A) various concentrations of AgPs loaded with 160µg/mL ampicillin and (B) control tests of AgPs loaded with PBS, Ps loaded with 200 µg/mL ampicillin, free ampicillin at a concentration of 1mg/mL, and no treatment (pure PBS). (C) Transmission electron micrographs reveal that the AgPs orient “silver nanoparticle first” in order to interact with the bacterial outer membrane (white arrows).

**COLL 342**

*Poly(1,2-glycerol carbonate)-graft-succinic acid-paclitaxel conjugate polymer for tunable nanoparticle delivery of paclitaxel*

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Biodegradable and biocompatible polymers have wide applications in biomedical research. Glycerol based polymers have gained increasing interest due to their biodegradability, biocompatibility, and amenability to functionalization and tuning. Poly(1,3-glycerol carbonate) based biomaterials have been explored in the development of drug delivery systems and coatings for medical implants. Recently, we have developed a method for the synthesis of linear atactic poly(1,2-glycerol carbonate)s with an easily modifiable structure. We herein describe the synthesis of a novel poly(1,2-glycerol carbonate)-graft-succinic-acid-paclitaxel (PGC-Pax) polymer which can be utilized for the synthesis of polymeric nanoparticles (NPs), and in which Pax can be incorporated at high loadings (>60 wt%). Additionally, the polymer backbone is readily degradable and biocompatible, with glycerol, succinic acid, and carbon dioxide as the degradation byproducts. Reducing the carrier material and maximizing the drug content departs from current Pax drug carriers that typically contain <10 wt% drug loading. Pax is one of the most widely used chemotherapeutic agents for a variety of solid organ malignancies (lung, ovarian, breast, head and neck cancers, and advanced forms of Kaposi’s sarcoma). However, despite its widespread use, Pax suffers from poor solubility, rapid systemic clearance, limited tumor exposure, and low target tissue concentrations (~0.4% of the systemically administered dose). Due to its poor aqueous solubility, Pax is often delivered in a Cremophor EL (C/E) adjuvant; and C/E itself is known to cause adverse side-effects and hypersensitivity reactions. We herein demonstrate the synthesis and in vitro characterization of PGC-Pax NPs with tunable release kinetics and in vitro cytotoxic activity. We also show the internalization of rhodamine labeled PGC-Pax (PGC-Pax-Rho) NPs in these cells via flow cytometric analysis and confocal microscopy.

**COLL 343**

*Structural and micellar stability of nanoscale amphiphilic polymers: implications for atherosclerosis bioactivity*
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Atherosclerosis, a leading cause of mortality in developed countries, is characterized by the buildup of oxidized low-density lipoprotein (oxLDL) within the vascular intima, unregulated oxLDL uptake by macrophages, and ensuing formation of arterial plaque. Amphiphilic polymers comprised of a branched hydrophobic domain and a hydrophilic poly(ethylene glycol) (PEG) tail have shown promising anti-atherogenic effects through direct inhibition of oxLDL uptake via macrophage scavenger receptors. Above a critical micelle concentration, these sugar-based amphiphilic polymers self-assemble into micelles with nanoscale sizes suitable for biomedical applications. While previous research has evaluated their colloidal stability and bioactivity *in vitro*, they have not yet been fully characterized under physiological conditions. To investigate their potency as atherosclerotic therapeutics *in vivo*, amphiphilic polymers with different linkage types were treated with lipase to study their structural stability given the abundant presence of lipase in human serum. Susceptibility to lipase-catalyzed hydrolysis can significantly reduce bioavailability *in vivo*. The stability of polymeric micelles in the presence of serum, provides insights into the integrity during circulation, was assessed by incorporating Förster resonance energy transfer pair as fluorescent probes. Finally, amphiphilic polymers’ ability to inhibit oxLDL uptake in macrophages under serum-containing conditions was compared to serum-free conditions to determine the influence of serum. These studies provided invaluable insights regarding the design of novel polymeric micelles as cardiovascular therapies.
Design of hybrid poly (lactide co glycolic) nanoparticles and in vivo fate studies for the assessment of nanoparticle degradation

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Polylactic co glycolic nanoparticles (PLGA NPs) with submicron size display excellent biodegradability and biocompatibility properties that make them very attractive as pharmaceutical carriers. Drugs can be encapsulated in the NP core during NP fabrication or assembled on top of the NP.

We will show the fabrication of hybrid PLGA NPs entailing magnetic iron oxide NPs and quantum dots that can be used for cell labelling and magnetically sorting. Based on the encapsulation or iron oxide NPs we will developed a dual-labeling strategy to assess simultaneously the pharmacokinetic properties and biological fate of PLGA NPs after intravenous administration in rodents was developed. PLGA NPs stabilized with Bovine serum albumin (BSA) NPs were simultaneously labelled with $^{111}$In in the core and $^{125}$I in the BSA coating. Both isotopes emit gamma rays with different energies (171 and 245 keV for $^{111}$In, 35.5 keV for $^{125}$I).

Biodistribution studies were performed applying Single-photon emission computed tomography (SPECT). Labelled NPs were administered via the tail vein and static images were acquired at different times after administration. Energy-resolved images to determine the loci of both isotopes over time were obtained. SPECT studies show a progressive accumulation of $^{125}$I in the thyroid glands, the intestine and the bladder, together with preferential accumulation of $^{111}$In in other major organs such as the lungs and the liver, suggest a fast degradation of the NPs after administration. Results were confirmed by organ harvesting and gamma counting.

The intracellular degradation of PLGA NPs by means of flowcytometry and Raman Microscopy will be studied as well.

Biodegradable polymer multilayer capsules for delivery of mRNA

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Viral vectors are efficient systems for nucleotide delivery but they encompass risks of mutagenesis, safety, immunogenicity, and high production costs. This has encouraged researchers to focus on alternative nonviral systems. Currently available cationic lipid-based delivery or cationic complexes of DNA / RNA are often highly toxic for the cells or not efficient for many cell types. In our study to encapsulate and deliver RNA, we propose biodegradable microcapsules by the layer-by-layer (LbL) technique. This technique is based on the sequential adsorption of oppositely charged molecules, such as polyelectrolytes, onto a charged sacrificial template. The template is then dissolved,
resulting in hollow capsules with a wall thickness in the nanometer range. Polyelectrolyte microcapsules (PEMs) have the advantages of mild preparation conditions, multifunctionality, and the capacity to encapsulate large amounts of material. Polyelectrolyte microcapsules are produced at room temperature using simple bench-top equipment, without organic solvents or harsh reaction conditions.

In the present study, we employed calcium carbonate microparticles as a sacrificial template. CaCO$_3$ microparticles represent “bio-friendly” tool for encapsulation of proteins and nucleic acids, enzymes and nanoparticles. Porous morphology of CaCO$_3$ offers large surface area and, thus, an opportunity to capture macromolecules with high efficiency. RNA was “pre-loaded” into the microspheres by coprecipitation in the process of their synthesis. Inorganic template extraction was performed after layer-by-layer coating by EDTA treatment. As outer shell, we used dextran sulfate (DS) and poly-L-arginine (PArg), which are known to be biodegradable polymers. The capsules prepared were tested for cellular non-toxicity and used for delivery of mRNA.

**COLL 346**

**Cell surface engineering for translational medicine: From single cell modification to disease theranostics**

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Cell surface engineering here as a avenue of research covers two points. Firstly, it is with the purpose of exploring the molecular structure of cell from a biological standpoint and secondly it aims at discovering the characterizations and prosperities of materials from the perspective of material science, such as surface topography and structure of ECM, particles size and shape, and so on. We developed an approach for cellular shellization, which provide a strategy to prolong the lifetime of yeast cells, and also a scaffold for chemical or biological modification of cells. Furthermore, universal red cells, which is antigenically shielded and as a potential strategy for blood transfusion applications, were also developed based on cellular interfaces. Besides, cell-materials interfaces are considered together for cell capture, such as circulating tumour cells sorting. Cell surface engineering give the prospective for single cell manipulation, which could find their applications in translational medicine, such as cell sorting for cancer diagnostics, cell therapy or delivery for therapies of invasion diseases.

**COLL 347**

**Investigating the impact of nanoconjugation on EGFR-induced apoptosis**

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Engineered nanoparticles are of great interest in many biological and medical applications. In many cases biomolecules are tethered to the nanoparticles to provide targeting and/or therapeutic functionalities. The impact of nanoconjugation, the covalent attachment of a biomolecule to a nanoparticle, on the functionality of the tethered ligand is, however, not well understood. The main objective of our research is, therefore, to investigate the effect of nanoconjugation on the mode of function of the epidermal growth factor (EGF) upon binding to its cellular target. Epidermal growth factor receptor (EGFR) is a tyrosin kinase that regulates cell proliferation and can cause cancer if dysregulated. Previous studies have indicated that covalent conjugation of EGF to gold nanoparticles can result in an enhancement of EGF induced apoptosis in EGFR overexpressing A431 and MDA-MB-468 cells. To elucidate the potential mechanisms underlying this enhancement, we investigated the intracellular spatio-temporal distribution of the EGFR bound nanoconjugated EGF (NP-EGF) and the EGFR activation as function of time using dynamic colocalization microscopy. Our studies reveal a profound impact of nanoconjugation on intracellular EGFR trafficking and indicate a delay of key events in EGFR signaling. The performed characterization of NP-EGF enhanced apoptosis contributes to an improved understanding on how nanoconjugation impacts the tethered surface ligand and provides new opportunities for overcoming apoptosis evasion in cancer cells.

COLL 348

Transferrin-modified single walled carbon nanohorns for selective uptake into cancer cells

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Transferrin is an iron carrying protein essential for cellular metabolism and transport of iron. The cellular receptor for transferrin is significantly overexpressed in the highly metabolic cancer cells, especially breast and bladder cancers. Due to this overexpression, the transferrin protein is an attractive targeting moiety for selective uptake into tumor cells. Single walled carbon nanohorns (SWNHs) are a relatively unexplored nanoparticle with a large surface area for modification, internal volume, and act as a photothermal agent for thermal treatment of tumors. In this investigation, we coupled SWNHs to transferrin along with a fluorescent tag (5(6)-FAM) for the formation of targeted molecular imaging particles (SWNH-Tf). Surface modification of oxidized SWNHs was achieved via carbodiimide coupling between carboxylic acid groups on SWNH surfaces and primary amines found on the protein and fluorescent tag. BCA assay confirmed the presence of transferrin protein on SWNH surfaces, and overlays of fluorescence imaging of stained transferrin and 5(6)-FAM indicates the presence of both groups simultaneously on SWNH-Tf surfaces. Cellular uptake of SWNH-Tf, evaluated via flow cytometry, showed an increase in particle uptake as a function of increasing
concentration in AY-27 rat bladder cancer cells (Figure 1). The comparison between MCF-7 and MCF-10A (transferrin receptor overexpressing and normal expressing breast cells, respectively) showed the activity of the SWNH-Tf in a transferrin-competitive environment. These SWNH-Tf have the potential to afford selective photothermal therapy in transferrin receptor-expressing tumors.

Figure 1. Cellular uptake of SWNH-Tf analyzed via flow cytometry of AY-27 rat bladder cancer cells incubated with no SWNH-Tf (red, left), 0.01 mg/mL solution SWNH-Tf (blue, middle), 0.1 mg/mL solution SWNH-Tf (orange, right).

**COLL 349**

**Differences between the surface properties of emerging aerogel biomaterials and planar substrates: Tuning cell/surface interactions on microporous materials for neuronal scaffolds using organic surface coating strategies**

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Limitations with existing methods and materials used for nerve repair necessitate the design and characterization of novel materials that can support electrical circuitry and promote controlled precise adhesion, growth, and directionality of neurons on artificial “smart” substrates and scaffolds. The overlapping long-term goal of the Alexander and Sabri groups is the development of designer biomaterials necessary for creation of
“smart” neuronal scaffolds. Currently, growth and adhesion-promoting coatings such as collagen, matrigel, and laminin are physically deposited (with a pipette) directly onto conductive gold-coated aerogel substrates without any bonding between the gold layer and the protein mixture necessary for neuron attachment and proliferation. This crude technique leads to uneven distribution of the coating, inconsistencies in the deposited layer thickness as well as possibilities of void regions. The coating thickness is heavily influenced by the morphology, roughness, and surface chemistry of the surface to be coated which will lead to local variations and inconsistencies in the attachment, growth, and extension of neurites by the neurons. It is therefore necessary to develop a reliable and reproducible mechanism that can covalently attach the peptides of interest directly to the gold layer. There exist decades of research study on functionalized alkanethiolate attachment/self-assembly to gold surfaces to form self-assembled monolayers (SAMs), which provides a robust and proven chemistry to achieve our coating goals. But can our extensive knowledge of planar SAM surface properties be transferred to microporous substrates such as microporous aerogels, which have shown promise as new biomaterials? This talk will focus on experimental and computational efforts to answer this question. Surface spectroscopy, material characterization, and molecular dynamics methods are employed to compare gold-coated aerogel surface properties to that of planar gold surfaces. These surface properties will be discussed within the context of tuning the surface to control overall cell/surface interactions.

COLL 350

**Impacts of surface modification induced by cold atmospheric plasma (CAP) on human mesenchymal stem cell (hMSC) differentiation**

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Three-dimensional (3D) printing is a new fabricating method for tissue engineering. The significant advantage of this new scaffold fabrication method is that it can precisely control scaffold architectures. However, scaffolds not only need 3D biocompatible structures, but they also require mimicking of the extracellular matrix properties of the tissue they intend to replace, such as providing a template for cell attachment, and to stimulate bone tissue formation in vitro [1]. In order to achieve the second target, the objective of the present in vitro study was to use cold atmospheric plasma (CAP) to modify a 3D printed scaffold’s surface roughness and chemical composition [2]. Under the optimized CAP conditions, the water contact angles of a poly-lactic-acid (PLA) scaffold dramatically dropped from 70±2° to 24±2° after CAP treatment. On the other hand, surface roughness also changed after CAP treatment via atomic force microscopy (AFM) measurements (Figure 1). The roughness (Rq) of the untreated scaffold, CAP treated scaffolds for 1, 3, and 5 min were 1.168 nm, 10.45 nm, 22.87 nm, and 27.60 nm, respectively. This means that the nanometric roughness had a maximum 250 %
increase. Both hydrophilicity and nanoscale roughness changes represented very efficient plasma treatment. When studying CAP treated 3D printing scaffolds, we indicated that the above surface property modification will lead to an enhancement of cell attachment and bone cell function. Those promising results suggest that CAP surface modification may have potential applications previously not thought of for enhancing bone tissue engineering applications.

References

Acknowledgement
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Figure 1. Cold atmospheric plasma (CAP) altered the topography of PLA scaffolds.

COLL 351

Protein films fabricated via nanoimprint lithography and inkjet printing: A new scaffold for cell patterning

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Proteins provide versatile and sustainable precursors for functional materials. Current approaches for generating stable protein films require either naturally self-assembling proteins or the use of additional crosslinking reagents. We report here a general
strategy for generating robust nanopatterned protein films using nanoimprint lithography. This approach provides control of the surface properties of the fabricated films through either the protein diversity or the choice of imprinting conditions. This control is demonstrated through the generation of films featuring vastly differing biological properties, with tunable biodegradability, surface charge, antifouling and cytophilicity. When combined with inkjet printing, spatial and compositional control of components within protein films can be achieved. This strategy should be generalizable to essentially all proteins, providing access to useful biomaterials, and more broadly to the creation of eco-friendly materials.

Different charged protein films fabricated via nanoimprint lithography (NIL) are used for controlling cell adhesion. The features generated by molds or inkjet printing can be used for directing cell growth

**COLL 352**

**Print surfaces with desired cell adhesion properties**

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Cell adhesion plays critical role in many biological processes. Cell migration, for example, begins with protrusion of cell membrane followed by the formation of new adhesions. Many physical and chemical factors affect the adhesion of cell, including hydrophobicity, surface charge, molecular interactions and surface roughness. While it is possible to create a surface with certain cell adhesion properties, control local cell adhesion environment at micro scale is still extremely difficulty. The challenge is to find out a method that is able to create any arbitrary distribution of surface properties at micro-scale level and possesses compatibility with a wide range of materials. As a step forward, we have developed a novel approach that is able to spatially control cell adhesion environment. Continuous generation of heterogeneous polymeric parts has been demonstrated and applied in fabricating cell adhesion surface and scaffold for...
the first time. An advanced projection microstereolithography (PuSL) system was used to fabricate features of interest, which readily allowed us to obtain most structures in minutes at micro-scale resolution. Surface properties of the as prepared objects were controlled during the polymerization process of 3D printing. For example, hydrophobicity variations across the surface were obtained through two mechanisms: (i) deposition of two or more materials at desired locations or (ii) change reaction conditions in a spatial manner to tune property of a pure material. Other parameters, such as surface roughness, charging state and surface functional groups can also be controlled with similar manner.

The method we show here is simple, cost efficient and highly reliable. It can be utilized to create any arbitrary 3D structures and is compatible with many polymeric and inorganic materials. We have fabricated several features with biocompatible materials, which showed selective cell adhesion at previously designed locations.
The extracellular matrix (ECM) is a complex system composed of an intricate network of proteins, polysaccharides and cells. There is a large variance in the ECM's mechanical and biochemical properties depending on the tissue or organ type. In this study, a hydrogel is developed to mimic soft tissue ECM (e.g., brain matrix) using hyaluronic acid as the backbone biopolymer. The hydrogel’s mechanical properties, such as shear storage modulus ($G'$), are directly modulated by the degree of crosslinking while its biochemical properties are controlled via incorporation of bioactive molecules. Adult human neural stem cells are maintained and differentiated within the hydrogels for multiple weeks. Cell viability and differentiation profiles are analyzed via live-cell microscopy (imaging) methods and biochemical assays.

COLL 354

Macromolecule solvent density distribution can be reconstructed from heteroatoms proximal radial distribution functions

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We consider the effect of sulfur, phosphorus, and charged side chain atoms on proximal radial distribution function (pRDF) of the water-solute pairs within the context of side chain analogs, nucleotides, a whole protein, and a double helix DNA. The pRDF represents the relative probability of finding any solvent molecule at a distance $r$ away
from the closest or surface perpendicular protein atom, \( g_{\perp}(r) \) and is the near neighbor
distribution. Previously, they were shown to be universal descriptors between water
molecules and the C, N and O atom types across hundreds of globular proteins. Using
these pre-computed pRDFs from water-small molecule pairs, a solvent density around
macromolecules can be reconstructed with modest relative error. Solvent reconstruction
using the additional information from charged amino acid side chain atom types, S, and
P atoms from small models reveal the unique effect of surface charge distribution on
solvent density. Macromolecule solvent density reconstructions from the small molecule
models better reproduce molecular dynamics simulations in terms of preferred hydration
sites and density fluctuation than those from larger systems where the next near
neighbors may change the relative contributions. Solvent distribution around a variety of
other moieties to consider post-translational modifications such as phosphorylation,
acetylation and disulfide bridge formation can be achieved.

Macromolecule solvent density is reconstructed from the small molecule models \( g_{\perp}(r) \)

**COLL 355**

*Enhancing supercapacitor energy-storage materials with sustainable, Earth-
abundant metals via nanoplates and molecular spacers*
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As demand for renewable energy such as solar, wind, and tidal increases, an efficient means for storing this energy must be available in order to make these systems cost efficient. Supercapacitors have shown to be a promising answer to this demand due to increased energy storage when compared to the common parallel-plate capacitor. Additional advantages include charge-discharge rates, cycle lives, and working-temperature range. However, some areas that need to be improved before practical use are the cell potential, specific energy, and production cost. To improve the specific energy of our supercapacitors, we use nanoplates of various mesoporous-metal oxides such as NiO and CoO and their mixtures to maintain ion transport. The use of SWCNTs or MWCNTs as spacers between the nanoplates contribute to enhance the power characteristics due to their high electrical conductivity. Moreover, we control the aggregation and thereby the ion-accessible surface area of the carbon nanotubes by binding novel metal coordination complexes to them. These Earth-abundant complexes act to enhance available Electrical Double Layer Capacitance and add a significant pseudocapacitance; increasing the specific capacitance, energy, and power. We will present results using molecular-spacer compounds such as [Ni(dibenzo[a,c]dipyrido[3,2-h:2',3'-j]phenazine)_3]^{2+} and 4-(tert-butyl)-2,6-bis((2-(phthalazin-1-yl)hydrazono)methyl)phenol (m$_2$-methoxo) dizinc(II) which use earth abundant metals. Structure of assembled SWCNT supraparticles and nanoparticle composites by electron microscopy, XRD, and light scattering will be presented. Redox properties of surface adsorbed assemblies and complexes by electrochemical and spectroelectrochemical methods will be presented. The capacitance of thin film composites were determined using standard electrochemical methods including galvanostatic charge-discharge measurements. Equivalent circuit analysis of the composite electrodes were measured using electrochemical-impedance spectroscopy. Experimental studies will be compared to computational modeling of these systems.

**COLL 356**

**Probing the mechanistic of charge transfer from optically excited plasmonic metal nanoparticles and adsorbates leading to chemical transformations**

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It has been demonstrated recently that optically excited plasmonic metal nanoparticles can induce chemical transformations. It has been proposed that these chemical transformations take place through a transfer of charge from the plasmonic catalyst to the adsorbate, leading to the charge-driven chemical transformations. While the general features of the process are reasonably well understood, there are certain aspects of the mechanism that are less clear. Among others, the nature of the interaction between the
localized surface plasmon states (LSPR) and electronic adsorbate states is still under debate.

In these studies, probe molecules were used along with silver nanoparticle catalysts in a number of Raman spectroscopy experiments to provide further insights into the mechanism of photo-chemical reaction on the surface of plasmonic metal nanoparticles. We will shed light on the nature of the interaction between localized surface plasmon states and the excited electronic adsorbate states and demonstrate how these interactions can lead to chemical transformations. We will discuss the implications of our studies on the chemical activity and selectivity of plasmon-mediated photo-chemical transformation on metal nanoparticles.


**COLL 357**

**Single molecule dynamics of a new class of altitudinal molecular rotors**

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Surface-bound molecular rotation can occur when the rotational axis is either perpendicular (azimuthal) or parallel (altitudinal) to the surface. The majority of molecular rotor studies involve azimuthal rotors whereas very few altitudinal rotors have been reported. In this presentation, altitudinal rotors are formed by means of coupling aryl halides through a surface-mediated Ullmann coupling reaction. All steps in the reaction on a Cu(111) surface are visualized by STM. The intermediate stage of the coupling reaction involves a metal-organic complex consisting of two aryl groups attached to a single copper atom. The phenyl rings are angled away from the surface which leads to unhindered rotational motion of substituent groups placed at the para position. Rotational events can be induced and quantified by electron tunneling current versus time measurements. We show how functionalization of the phenyl ring changes the energy barriers to rotation and perform an extensive set of inelastic electron tunneling driven rotation experiments. This tunable system offers an ideal platform for examining many fundamental aspects of the dynamics of molecular rotor and motors.

**COLL 358**
Influence of metal vacancy of undoped anatase TiO₂ on p-type conductivity, room-temperature ferromagnetism, and remarkable photocatalytic performance

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Defect engineering is important to tune the functional properties of metal oxides, such as electronic structure, charge transport, and catalytic performance. Compared with the often studied oxygen vacancies, the effect of metal vacancies on the physiochemical properties is seldom reported. Herein, we successfully synthesized undoped anatase TiO₂ abundant with Ti vacancies (9.5 mol%) by solvothermal treatment of tetrabutyl titanate in an ethanol-glycerol mixture and then calcination. Both experimental measurements and DFT calculations on cell lattice parameters prove the presence of V_Ti in the defected TiO₂. The presence of abundant V_Ti changes the charge density (Figure 1a) and valence band edge of TiO₂, makes the c axis of anatase shrink heavily, and generates an unreported strong EPR signal at g = 1.998 even under room temperature (Figure 1b). Contrary to normal n-type and nonferromagnetic TiO₂, Ti-defected TiO₂ shows inherent p-type conductivity (Figure 1c) with high charge mobility, and room-temperature ferromagnetism (Figure 1d) stronger than Co-doped TiO₂ nanocrystalline. Moreover, Ti-defected TiO₂ exhibits remarkably higher photocatalytic performance than normal TiO₂ in H₂ generation (4.4-fold, Figure 1e) and organics degradation (7.0-fold for phenol) because of the more efficient charge separation and transfer in bulk and at semiconductor/electrolyte interface, which was confirmed by DFT calculations and experimental results. In addition, the surface defects are stable under the reaction conditions and long-term storage. This work demonstrates that metal vacancies can change the structure characteristics and physiochemical properties of undoped semiconductor and thus produce a new kind of functional materials for chemical and physical devices.
Figure 1. (a) Charge density difference of defected and normal TiO$_2$. (b) Room temperature EPR spectra. (c) and (d) Mott–Schottky plots and magnetization(M–H)curves of defected TiO$_2$, respectively. (e) Time course of H$_2$ generation.

**COLL 359**

**Calculated photoinduced interfacial electron transfer of Fe(II) light harvesters on TiO$_2$ nanocrystals**

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Adsorption of molecular systems onto nanostructured surfaces is a crucial step for utilizing any promising complexes for solar energy conversion. The recent push for earth abundant transition metal complexes with improved energy level structures has led to iron-$N$-heterocyclic carbene complexes that exhibit more than 100-fold increases in room temperature lifetimes of metal-to-ligand charge transfer excited states over
traditional iron(II)-polypyridyl complexes. The usefulness of these promising Fe(II) complexes for light harvesting applications depends critically on the energy and lifetime of the $^3$MLCT excited state, as well as the alignment of the excited state to relevant electron acceptors and redox recovery mediators. Each new complex studied experimentally is costly and time consuming, ideally computational methods are a useful screening tool. Recent efforts to investigate excited state effects beyond the Franck–Condon region included unrestricted DFT (uDFT) optimizations of relevant minima and construction of projected potential energy surfaces as well as uDFT and time dependent (TD) DFT calculated potential energy surfaces of the lowest triplet state (T$_1$), provide information about activated decay pathways after the initial photexcitation. Quantum chemical calculations of dye-sensitized materials such as nano-TiO$_2$ furthermore provide opportunities to investigate interfacial electronic properties and charge transfer rates in significant detail. By relaxing an Fe(II)-carbene adsorbed on a TiO$_2$ nanocluster we show large driving force for injecting electrons from an Fe(II)-core to the conduction band of TiO$_2$, thus providing a computational prediction of the viability of Fe(II)-NHC complexes as efficient sensitizers for solar energy conversion applications.

Coll 360

Photocatalytic CO$_2$ reduction under periodic illumination of ZnS colloids

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The photoreduction of CO$_2$ to formate in sphalerite (ZnS) aqueous suspensions is studied in the presence of Na$_2$S hole scavenger. The rate of formation of formate is measured using cut-off filters at $\lambda_{\text{cut-off}} \geq 280, 295, 305, 320,$ and 400 nm. The dependence of the measured reaction rates on $\lambda_{\text{cut-off}}$ indicates that a wavelength of $\lambda = 345$ nm is associated with the actual bandgap of the colloidal suspension in water. The apparent quantum yield is measured under periodic illumination and suggests that (1) valence-band holes on the surface of ZnS disappear within deciseconds due to the oxidation of the scavenger while simultaneously pumping electrons to the conduction band, (2) excited electrons in the conduction band of ZnS are transferred to CO$_2$ to produce the intermediate CO$_2$•–, and (3) CO$_2$•– abstracts a proton from water and undergoes further photoreduction on the surface of ZnS in an overall time scale for steps 2 + 3 of a few milliseconds. The separation of both process merges at $\sim$29 ms because it decreases exponentially with a drop in [Na$_2$S] accompanied by a less negative surface potential. The behavior of the reaction rate at variable pH resembles the fraction of dissolved CO$_2$, discarding the direct participation of bicarbonate and carbonate in the reaction. Combined chromatographic, mass spectrometry, and spectroscopic studies provide new insights to understand the role of surface chemistry on the photoreduction of CO$_2$ on ZnS nanocrystals.

Coll 361
Controlling surface deposition of gold nanoparticles for the fabrication of highly porous silicon membranes via metal-assisted chemical etching

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Metal-assisted chemical etching is a recently developed technique in which noble metals facilitate the anisotropic chemical etching of crystalline silicon in a solution of hydrofluoric acid and hydrogen peroxide. Etching proceeds through electrochemical charge transfer between the silicon substrate and hydrogen peroxide, resulting in a local transformation of silicon to silicon dioxide, which is rapidly consumed by hydrofluoric acid. By utilizing nanoparticles as catalysts, it is possible to fabricate silicon membranes with high aspect ratio, sub 5nm diameter pores. Such nanoscale structures offer numerous benefits for applications such as phonon scattering in thermoelectrics, anti-reflection coatings in optoelectronics, and prototype nanoporous membranes for ultra-permeable filtration. In order to realize this potential however, the size, depth, spacing, and geometry of the nanopores must be both highly controllable and uniform.

Here we investigate a method for the deposition of gold nanoparticles from colloidal solution on a crystalline silicon substrate with highly uniform and controllable inter-particle spacing. This is done via the solution functionalization of gold nanoparticles with long chain alkanethiol ligands of various lengths. The alkanethiols serve both to prevent undesirable aggregation or clustering of the nanoparticles on the silicon surface, and to precisely control the inter-particle spacing. Following the optimization of the deposition process, the substrate is immersed in the etchant in order to evaluate the effect of the alkanethiol ligands on the etching process, specifically the etching rate and resulting pore morphology. Importantly, this process is tailored to achieve maximum porosity by minimizing ligand length while still attaining the desired spacing effect. Decreased ligand lengths are also expected to provide minimum resistance to pore formation, as etching proceeds via an electron transfer process between the substrate and nanoparticle. Surface chemistry of the gold nanoparticles before and after exposure to the etchant solution is probed via Raman and x-ray photoelectron spectroscopy, while particle spacing, array uniformity, and resulting pore morphology are characterized by high resolution scanning and transmission electron microscopy. This methodology enables us to finely control the spacing of nanoparticles on the silicon surface, while also revealing the morphology, uniformity, and aspect ratio of the resultant pores.

**COLL 362**

Corona phase molecular recognition of fibrinogen

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Corona Phase Molecular Recognition (CoPhMoRe) is a method whereby a heteropolymer is adsorbed onto a nanoparticle surface, templating it for the recognition of a specific target analyte. Recently demonstrated for small molecules\textsuperscript{1,2}, CoPhMoRe has not yet been shown to work for macromolecules such as proteins. In this work a CoPhMoRe screen of single walled carbon nanotubes (SWNT) wrapped in a library of phospholipid-poly ethylene glycol derivatives and oligonucleotides against a panel of human blood proteins reveals a phase highly selective to fibrinogen\textsuperscript{3}. This corona phase has one of the highest relative coverage of the nanotube surface, of more than 87\%, and upon the interaction with fibrinogen, a 54\% decrease in fluorescent emission intensity is observed. The three nodules of fibrinogen are shown to bind sequentially in a three step mechanism, with equilibrium constants that increase with the SWNT diameter, ranging from 3.5 nM for the (6,5) chirality to 31.4 nM for the (11,3) chirality. Protein CoPhMoRe is a promising method for recognizing specific bio-macromolecules, proteins, and peptides, for biological applications.


\textbf{COLL 363}

\textbf{Adhesion of cerium oxide nanoparticles on supported lipid bilayers: Implications for nanoparticle–membrane interactions}

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The adhesion of cerium oxide (CeO\textsubscript{2}) nanoparticles (NPs) to cell membranes is an important step for initiating the cytotoxicity of CeO\textsubscript{2} NPs. Thus, it is important to understand the interactions between CeO\textsubscript{2} NPs and cell membranes. In this study, the propensity of CeO\textsubscript{2} NPs to adhere to model cell membranes, 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) supported lipid bilayers (SLBs), was evaluated by deriving deposition attachment efficiency of CeO\textsubscript{2} NPs on SLBs. The impact of pH, valance of electrolyte, and electrolyte concentration of ambient solutions on the attachment efficiency of CeO\textsubscript{2} NPs on SLBs was investigated. The isoelectric points of DOPC membranes and CeO\textsubscript{2} NPs were determined to be pH 4.2 and 7.2, respectively. At pH 8.0, both SLBs and CeO\textsubscript{2} were negatively charged. The attachment efficiency increased with NaCl concentration due to charge screening effect of Na\textsuperscript{+} cations and also increased with CaCl\textsubscript{2} concentration due to charge neutralization and charge reversal effects of Ca\textsuperscript{2+} cations. The critical deposition concentrations (CDCs) (i.e. the lowest
electrolyte concentration at which favorable deposition occurs) of NaCl and CaCl₂ are 11 and 0.62 mM, respectively. At pH 2.0 and 4.0, both CeO₂ NPs and cell membranes were positively charged. The attachment efficiency at both pHs increased with NaCl and CaCl₂ concentrations due to the charge screening effect of Cl⁻ anions. At the same electrolyte concentration, attachment efficiency at pH 2.0 is mostly higher than that at pH 4.0, because cell membranes are more positively charged at pH 2.0 than at pH 4.0 and thus exerting higher electrostatic repulsion on approaching CeO₂ NPs. At pH 5.5, however, CeO₂ NPs and cell membranes were oppositely charged. The electrostatic attractions between CeO₂ NPs and cell membranes rendered the attachment of CeO₂ NPs favorable regardless of electrolyte concentrations. In addition, the reversibility of CeO₂ NPs adhesion was examined following their attachments to cell membranes. It was found that most of deposited CeO₂ NPs were not able to be released from cell membranes upon rinsing with low ionic strength solutions at all tested pHs. It is speculated that the energy barrier of release for CeO₂ NPs was still high enough to prevent most CeO₂ NPs from detaching from cell membranes even at a very low ionic strength.

COLL 364

Chemo-enzymatic routes to lipopeptides and their colloidal properties

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A unique chemo-enzymatic route to lipopeptides was demonstrated herein that, relative to alternative methods such as SPPS and microbial synthesis, is simple, efficient and scalable. Homo and co-oligopeptides were synthesized from amino acid ethyl esters via protease catalysis in an aqueous media, followed by chemical coupling to fatty acids to generate a library of lipopeptides. Synthesized lipopeptides were built from hydrophobic moieties with chain lengths ranging from 8 to 18, and peptides consisting of oligo(L-Glu) or oligo(l-Glu-co-L-Leu) with an average of 7 to 8 repeating units. The chemical structures of the lipopeptides were characterized and confirmed by NMR and MALDI. The colloidal and interfacial properties of these lipopeptides were characterized and compared in terms of the hydrophobic chain length, oligopeptide composition and solution pH. The results showed correlation between the interfacial activity of the lipopeptides and the hydrophobicity of the fatty acid and oligopeptide head-group, the effect of which have been semi-quantitatively described in the manuscript. Results from these studies provide insights into design principles that can be further expanded in future work to access lipopeptides from protease-catalysis with improved control over sequence and exploring a wider range of peptide and lipid compositions to further tune lipopeptide biochemical and physical properties.
Preparation of long (~7.2kb) DNA origami scaffold using PCR and lambda exonuclease digestion

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In addition to carrying the genetic code for life, DNA can also be used as a generic building material for nanostructures. Numerous DNA nano-objects of various sizes and shapes have been built based on the ~7.2kb long M13mp18 ssDNA plasmid through DNA self-assembly. Recently some short DNA plasmids or genomic amplicons have been used to prepare small nanostructures, however to develop the standard size (~70 nm x 90 nm, though the shapes may vary) DNA nanostructure using different genomic ssDNA scaffolds, the development of a quick and efficient method to prepare long ssDNA (~7.2kb) scaffolds has remained a challenge. To address this challenge, a PCR based approach has been developed using Q5® High-Fidelity DNA Polymerase (NEB). The DNA sense strand (ssM13mp18 strand) of the amplicon was labeled with a 5¢-phosphate group to make it a viable target for λ-Exonuclease digestion (Fig. 1a). The yield of the anti-sense ssDNA digestion product was ~90%. Rectangular origami (97nm x 76nm) was successfully prepared (Fig. 1b) and the longer edges self-annealed to form (97nm x 24nm) tube-like origami (TO) shown in Fig. 1c. Finally, one-dimensional TO was prepared by annealing individual TO together by adding staples with single stranded overhangs (sticky ends), demonstrated in Fig. 1d.
In summary, we have developed and demonstrated the use of a simple and general scaffold preparation method for forming DNA nanostructures, which will open the way for fabrication of a rich diversity of DNA nanostructures designed to meet the increasingly precise requirements of structural nanoscale research. This work was funded by NSF Cooperative Agreement Number EPS-1003907.

Figure 1. a) Generation of scaffold by PCR and lambda exonuclease digestion, PCR reactions were performed using double stranded m13mp18 as a template. The sense primer had a 5’phosphate group for λ-exonuclease digestion. The anti-sense primer had 5’phosphorothioate bonds to protect the anti-sense strand from digestion. PCR product was digested, leaving the anti-sense strand; the product (b) rectangular origami can be rolled into (c) tube origami, which can subsequently be combined into (d) one dimensional tube origami

**COLL 366**

**Design and synthesis of synthetic antibodies, CoPhMoRe and the inverse CoPhMoRe problem** for helically wrapping polymers on single-wall carbon nanotubes

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Corona Phase Molecular Recognition (CoPhMoRe) is a new technique that generates a nanoparticle coupled polymer phase capable of recognizing a specific molecule with high affinity and selectivity. CoPhMoRe has been successfully demonstrated using polymer wrapped single walled carbon nanotubes, resulting in molecular recognition complexes, to date\textsuperscript{1,2}, for dopamine, estradiol, riboflavin, L-thyroxine, and the protein fibrinogen, utilizing combinatorial library screening. A rational alternative design to this empirical, library screening is to solve the mathematical formulation that we introduce as the CoPhMoRe inverse problem. This inverse problem seeks a linear function representing the position of monomers or functional groups along a polymer backbone that results in a 3-dimensional structure capable of recognizing a specific molecule when mapped to a nanoparticle surface. The potential solution space for such inverse problems is in general infinite, but for the specific constraint of a helically wrapping polymer, mapped to a cylindrical nanoparticle, we will show in this talk that two types of inverse solutions are exactly solvable. In one case, the polymer pitch and composition can be designed to allow for the specific binding of a small molecule analyte in the occluded space on the nanotube surface. In the other, a larger macromolecule can interact with a deformed helix, which partially conforms to it. A highly simplified, coarse grained molecular model of a helically wrapping polymer demonstrates the inhomogeneous binding potential formed by the wrapping with a given pitch. Varying the pitch illustrates that there is an optimal value that enables the selective and specific binding of a target analyte. While these are idealizations of actual CoPhMoRe phases, the formation and solution of such inverse problems may serve to reduce the dimensionality of library screening for CoPhMoRe discoveries, as well as to provide a theoretical basis for understanding certain types of CoPhMoRe recognition.


COLL 367

Nanopore entry of proteins and macromolecules

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The ca. 50 nm pores of the nuclear pore complex directs all protein and RNA traffic between the cell nucleus and the cytoplasm without direct energy input, and shows that a polymer functionalized nanopore can enable selective macromolecular transport. Towards the design of synthetic versions of such chemically selective nanopores, we investigated the combined roles of steric exclusion and surface charge in the diffusion of macromolecules into the nanopores of anodic alumina with initial diameters 30–100 nm. Layer-by-layer (LbL) deposition was used to define the surface charge and to achieve precise control over the final pore diameter. The pore entry of a number of proteins, dendrimers and linear polymers of similar hydrodynamic radii were sensitively
monitored *in situ* using nanoporous optical waveguide spectroscopy. As expected, nanopore entry was uninhibited with relatively large pores. However, the inhibition of pore entry with decreasing pore diameters occurred at a pore size that is still several times the diameter of the charged macromolecule. Control experiments at various ionic strengths and on an unstructured planar surface, as well as coarse grain modeling, show that the nanopore entrance likely provides a geometry that produces effectively an enhanced surface charge effect. The phenomenon may be applied towards protein separation as well as the preferential functionalization of the internal and external surfaces of a nanoporous membrane.

**New stimuli responsive lipid nanotube for protein transport and release: From molecular design to application**

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Lipid nanotubes have various advantages such as high biocompatibility, simple production, high inner volume etc. which make them preferential especially as carriers for different guests. Here, the usability of the recently designed AQUA (AQ-NH-(CH$_2$)$_{10}$COOH, where AQ is anthraquinone) nanotubes for protein transport and release is investigated. The loading capacities and release profiles of hemoglobin (Hb) and BSA (Bovine serum albumin) proteins are determined. Due to the tubular geometry and the rational molecular design, relatively higher loading capacities are achieved. The π-π stacking, electrostatic and hydrogen bonding interactions, provided by AQ and COOH groups existing on the nanotube walls, contribute this high entrapment efficiency. The loading capacities and release profiles change with pH and temperature. AQUA nanotubes release a high portion of the entrapped BSA in a pH and temperature...
controlled manner, but, the released Hb amount is very low. Those properties are attributed to the smart design of AQUA molecule. The quite high and low release amounts for BSA and Hb are both promising for different purposes and reveal the usability of AQUA nanotubes in the controlled release and artificial blood applications, respectively.

COLL 369

Fibrinogen adsorption and relaxation kinetics and silica particle capture on graphene-modified glass

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Towards the creation of devices that can capture and communicate with targeted analyte particles and cells, this project examines the fundamental colloidal interactions between proteins or silica microspheres and single (or nearly single) epitaxially grown graphene sheets transferred to a flat silica glass support. These interactions are compared with those of protein and silica microspheres interacting with flat bare silica and hydrophobic surfaces. In this study, fibrinogen adsorption was examined as a function of concentration and flow rate, and extensive protein adsorption and retention was found on all surfaces. Additionally, an analysis of the average protein footprint, obtained from the ultimate coverages, as a function of effective surface residence time provided perspective on interfacial protein reconformation, and possibly denaturing, which was more extensive on graphene and hydrophobic surfaces. Furthermore, while the impact of ionic strength on the capture of flowing silica spheres is adequately described by DLVO theory, we report a surprising parallel but weaker influence of ionic strength on silica sphere interaction with supported graphene. The latter suggests the presence of interfacial charge at the graphene-water interface either through ion adsorption or from a small number of oxidized groups on the graphene, which do not appear to contribute to protein adsorption.
COLL 370

Multimodal nanobiocatalysis: Toward the synthesis of pharmaceutically relevant enantiopure drugs and drug intermediates

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Biocatalysis has become a new vehicle for chemists to reach their scientific destiny through an economical and safe journey. Combination of nanomaterials along with biocatalysts has added advantage of prolonged use of biocatalysts. Immobilization of biocatalytic enzymes on multiple nano-scaffolds (e.g. multiwalled carbon nanotube) was successfully achieved. Optimization of various reaction parameters (reaction time, temperature, concentration of the substrates used and pH) for immobilization was achieved by using statistical design methods. Nanobiocatalytic approach used for the immobilization of biocatalytic enzymes on nanomaterials made the enzymes more stable and more efficient compared to the free enzymes. Use of a statistical design technique for the optimization of enzyme immobilization parameters makes this study statistically more significant.
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Interaction of graphene oxide with bacterial cell membranes: Insights from AFM-based force spectroscopy

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Understanding the interactions of graphene oxide (GO) with biological membranes is essential for the evaluation of GO’s health and environmental impacts, and to advance graphene-based biological and environmental applications. Toward this goal, we used atomic force microscopy to investigate the forces between surface-immobilized *E. coli* cells and AFM probes functionalized with GO. GO-cell interactions were found to be primarily repulsive. Our force spectroscopy results suggest that physicochemical interactions do not underlie the primary mode of action of GO in bacteria.

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Noncovalent approach for developing hybrid mesoporous silica nanoparticle-peptide amphiphile system

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Mesoporous silica nanoparticles (MSNs) with their specific features such as high specific surface area, large pore volume, controlled particle size and morphology, and low inherent toxicity have caught great attention of the scientific community. They serves as promising platforms for theranostics applications.\textsuperscript{1-3} To enhance their cellular uptake, cell targeting, bioimaging, and controlled drug release, the surface of mesoporous silica nanoparticles (MSNs) have been modified by using distinct moieties such as polymers (e.g. PEG and zwitterionic copolymers), small molecules (e.g. phosphonate) or biomolecules (e.g. antibodies, peptides, lipid bilayers, DNA and aptamers. Especially, peptides composed of short amino acid sequence have attracted great deal of attention in recent years because of their versatile functionality, biodegradability and biocompatibility. They are generally attached to the silica surface through covalent interactions which brings about low surface grafting density and high costs.

In this study, it was presented a simple and cost-effective self-assembly approach to develop peptide functionalized MSNs, as a promising alternative for covalent attachment methods.\textsuperscript{4} (Scheme 1) Driving force in the formation of peptide amphiphile (PA) integrated octyl modified MSN surfaces is the hydrophobic interactions between octyl groups of MSNs and alkyl chains of PAs. Two model PA molecules with different charges were selected for the modification of the MSN surfaces. Cell viability and uptake were evaluated before and after PA integration by using human umbilical vein endothelial cells (HUVEC) and a vascular smooth muscle cell line (A10).

REFERENCES

Scheme 1. Functionalization of octyl modified hydrophobic mesoporous silica nanoparticles with peptide amphiphile molecules
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Nanotribology of a catechol-functionalized alkane with terminal chain branching

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A bio-inspired system was studied where the terminal chain branching found in fatty acids naturally present on hair and wool was combined with a catechol group as the hydrophilic moiety to mimic the adhesion strategies found in mussel proteins. Atomic force microscopy (AFM) was used to study the adhesion and nanoscopic friction of monolayers of a catechol-functionalized branched alkane, 4-[(18S)-18-methyleicosyl]benzene-1,2-diol, formed by Langmuir-Blodgett deposition on silicon oxide, mica, and polydimethylsiloxane (PDMS) substrates. Measurements were done in ambient air and in dry N₂ gas. In dry N₂, the friction of these monolayers was low and the adhesion was well described by van der Waals interactions. In ambient air, the adhesion and friction showed a stronger hysteresis and different friction responses at low and high loads. The results will be discussed in view of possible bonding to the substrate and lateral cross-linking in the monolayer.

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Chiroplasmonic nanoparticles and their assemblies

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Many inorganic chiral nanoscale systems had been discovered over the last decade. They include individual nanoparticles with chiral tetrahedral geometry, DNA-based NP assemblies, helical nanowires and lithographically defined chiral nanoscale patterns. The latest data on chirality transfer from circularly polarized photons to nanoparticles and their helical assemblies that could be of particular interests to researchers in this Symposium. The origin of the exceptionally strong polarization rotation in many of plqaqsmonic nanoscale systems will be highlighted and substantiated by several experimental data sets. Special effort will be placed on the translation of unique structural and optical properties of chiral nanoscale materials to applications. It will be exemplified by the bioanalytical applications for detection of DNA oligomers using CD spectroscopy that enables 1-3 order of magnitude improvement of detection of protein, DNA oligomers, and small chiral molecules (Fig 1). Other technological applications in chiral catalysis and optical devices for telecommunication will be discussed as well.
Nanoparticle synthesis, surface modification, and colloidal dispersion facilitated by polymer amphiphiles

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Amphiphilic molecules such as surfactants and block copolymers afford nanoscale environments of varying and tunable shape, dimensions, mobility, local polarity, local concentration, and reactivity. Amphiphiles can thus nucleate or initiate nanoparticle (NP) formation, facilitate or arrest NP growth, and control NP size and shape. Amphiphiles can be further useful in surface-modifying NPs for dispersibility and compatibility, and in promoting long-range NP organization when coupled to ordered structures formed by the amphiphiles. The presentation will highlight findings from our research on the (a) size- and shape-controlled synthesis of NPs in aqueous solutions containing amphiphiles and inside self-assembled amphiphile templates, (b) surface-modification and colloidal dispersion of nanoparticles through adsorption of amphiphiles, and (c) incorporation of nanoparticles in ordered amphiphile matrices. The design of hybrid amphiphile+nanoparticle systems can be informed by such interplay between amphiphile self-assembly and NP properties.
Click assembly of nanoparticles into colloidal polymers

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Nanoparticles represent a new family of fundamental building blocks. Hierarchical assembly of nanoparticles into macroscopic materials may lead to novel materials properties but remains extremely challenging. Colloidal "molecules" comprised of discrete clusters or chains of nanoparticles may serve as the mesoscale structural units of more complex functional materials. Here we demonstrate that directed-assembly of nanoparticles into well-defined “molecular” architectures is possible via “click” reactions. We will discuss our preliminary data on creating bonding structures on Au nanorods by modifying their surfaces with heterogeneously functionalized polymers bearing complementary “click” reactive moieties. Highly selective and efficient “click” reactions are then conducted to covalently organize Au nanorods into colloidal “polymers”. We expect that these “molecular” architectures can be tuned via synergistic control of linker sizes and reaction stoichiometry. We will also discuss the broad utility of this method to assemble nanoparticles of different sizes and shapes.

COLL 377

Polymer-induced lipid cluster formation: Effects of charge density, curvature, lipid composition and polymer concentration

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Hydrophobic-hydrophilic interaction among amphiphilic molecules has been observed ubiquitously in nature and is essential for constructing unique morphology of complicated systems. We have studied the interaction between triblock copolymers (polypropylene-polyethylene-polypropylene) and uniform-sized (50 ~ 80 nm) unilamellar vesicles extruded from a solution containing a long-chain (dipalmitoyl) and a short-chain (dihexanoyl) phosphatidylcholine. The amphiphilic polymer can “string” the vesicles into large clusters in solutions. The preliminary data obtained from dynamic light scattering and UV-vis absorption measurements indicate that the observed clustering rate strongly depends on the charge density, curvature and lipid composition of the vesicles as well as the polymer concentration. Discussion over each parameter will be presented.

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Synthesis and characterization of the structure and activity of gold nanoparticles when coated with of poly (oxonorbornene)-based synthetic mimics of antimicrobial peptides (SMAMPs)

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Gold nanoparticles wrapped with polyelectrolytes have been used to stabilize the nanoparticles and to enable their applications in biological systems. Polyallyl amine hydrochloride (PAH) has been used frequently for this purpose. However, recent studies have indicated that PAH coated gold nanoparticles have adverse impact on phospholipid vesicles and cells. The impact of PAH-coated particles was found to be larger than the impact of free PAH on the phospholipid membrane. The surprising impact may be explained by the increase in the density of positive charges on the nanoparticle surface. In this study we make use for the first time of poly (oxonorbornene)-based synthetic mimics of antimicrobial peptides (SMAMPs), a promising new class of antimicrobial polymers with cell-selectivity and low resistance development potential. These hydrophilic SMAMP polymers were previously found to be 'doubly selective', i.e. they are not only selective for bacteria over mammalian cells, but also for Gram-positive over Gram-negative bacteria. The goals of our studies are: a) demonstrate that it is possible to coat gold nanoparticles with SMAMPs and that these novel nanoparticles are as or more stable than PAH-coated gold nanoparticles in aqueous solutions of increasing complexity. Preliminary data from recent experiments in our laboratory indicate that realizing this goal is feasible; b) demonstrate that SMAMPs-coated gold nanoparticles have lower impact on phospholipid vesicles and mammalian cell membranes when compared to PAH coated gold nanoparticles. Our study makes use of a combination of analytical methods to characterize the physical and surface chemistry of the polymer-coated gold nanoparticles, including UV/VIS absorption spectroscopy to determine the impact of polymer coatings on the plasmonic properties of the nanoparticles, and dynamic light scattering (DLS) and transmission electron microscopy (TEM) to characterize their aggregation state. Fluorescence methods are used to monitor the interactions between the polymer-coated gold nanoparticles and phospholipid molecules and cells.

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Synthesis of nanobowls with a Janus template

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Colloidal particles with two or more different surface properties (Janus particles) are of interest in catalysis, biological imaging, and drug delivery. Eccentric nanoparticles are a type of Janus particle consisting of a shell that envelops the majority of a core particle, leaving a portion of the core surface exposed. Previous work to synthesize eccentric nanoparticles from silica and polystyrene have only used microemulsion techniques. In contrast we report the sol-gel synthesis of eccentric Janus nanoparticles composed of a silica shell around a carboxylate-modified polystyrene core (Janus templates) and examine different reaction conditions in order to understand the mechanism of formation. In addition, we have synthesized nano-bowl-like structures after the removal of the polystyrene core by organic solvent. These Janus templates and nanobowls can be used as a versatile platform for site-specific functionalization or controlled theranostic delivery.

A silica bowl can be grown using a modified silica sol-gel process around a carboxylated polystyrene bead.

**COLL 380**

**Synthesis and Investigation of thermoresponsive core shell nanoparticles**

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Iron oxide nanoparticles have gained a lot of interest in the biomedical field with applications such as hyperthermia, drug delivery, cell labeling or as contrast agents. In combination with thermoresponsive polymer shells, e.g. poly(N-isopropylacrylamide) or poly(ethylene glycol), they can be further tuned to generate multiresponsive materials displaying a switchable shell collapse and expansion, triggered by thermal actuation. This opens exciting opportunities for superparamagnetic iron oxide particles, which can produce heat locally through interaction with alternating magnetic fields, to be used as building blocks for e.g. thermoresponsive membranes or triggered release vehicles. We prepared monodisperse and monocrystalline iron oxide nanoparticles in the size range...
of 3-12 nm in reproducible manner by thermal decomposition of iron pentacarbonyl in the presence of oleic acid. Thermoresponsive polymers (Mn: 5000-20000 g/mol) were modified with nitrocatechols and subsequently used for “grafting to” reactions with the oleic acid coated iron oxide nanoparticles. Dispersant densities of up to 0.8 chains/nm² were achieved by this method, which is limited by the coil size of the applied polymer. Higher grafting densities were achieved with a “grafting from” approach using surface initiated ATRP or a multistep “grafting to” reaction (up to 3 chains/nm²). The generated core shell structures display magnetic and thermoresponsive properties (LCST). The thermoresponsive behavior of the shell was monitored by DLS and SAXS. The combination of the techniques allowed for investigating both aggregation and internal shell structure as function of temperature stimuli.

(4) Zirbs, R.; Lassenberger, A.; Vonderhaid, I.; Reimhult, E. Nanoscale submitted

COLL 381

In-situ investigations of the interaction of small molecules with Fe²⁺-substituted MOF-5

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The M₄O(carboxylate)₆ secondary building units (SBUs) in MOF-5 can be regarded as unique C₃-symmetric tetracoordinating all-oxygen dianionic chelating ligands for a variety of divalent metal ions of the first row transition metal series. Various spectroscopic techniques applied to the Fe²⁺-substituted MOF-5 show that these SBUs not only display inherent flexibility, but also engender unique binding and reactivity with small molecules such as N₂ and NO. The very reactive, yet site-isolated nature of these high-spin ferrous Fe centers enables reactivity reminiscing that of enzymes, and also allows the isolation of very unusual reactive intermediates that have not been observed thus far in either enzymatic or heterogeneous catalytic reactions. The opportunities offered by MOFs in these and related areas will thus be discussed from the perspective of our results with Fe²⁺-substituted MOF-5.

COLL 382
Core-shell nanoparticles: In situ surface monitoring by Synchrotron X-ray spectroscopy

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Typical catalysts of the main industrial processes, such as Fischer-Tropsch Synthesis (FTS) or CO₂ reduction reaction, are complex both in terms of structure and composition. They often include several active metals and their properties are dependent on the size dispersion and support. This complexity is the key to develop selective catalytic reactions.

A recent trend in catalyst design consists in preparing well-controlled core-shell nanoparticles: they provide a good model for exploring the relationships between structure, composition, and selectivity, in the reactions of CO or CO₂ with H₂. These reactions are at the cross-road of synthetic fuel production and high-value chemicals preparation (eg. alcohols, ketones...). The main difficulty lies in the various restructuring that can happen to a bimetallic nanoparticle exposed to reactive gases: metal segregation, surface poisoning, partial oxidation, coking... will occur depending on the nature and morphology of the core-shell nanoparticles, and will strongly affect the reaction outcome.

As an in situ characterization tool, near ambient pressure x-ray photoelectron spectroscopy provides unique insights regarding these dynamic processes, as it allows following simultaneously the metals (oxidation state and surface composition) and the adsorbates (gas molecules, nanoparticles surface ligands).

At the Advanced Light Source in Berkeley, we monitored in situ the structural and chemical transformations happening to core-shell nanoparticles. Bimetallic nanoparticles (NiCo) were exposed to model reaction conditions (O₂, H₂, CO₂ and mixtures), evidencing the formation of a NiCo surface alloy under reducing conditions. In conjunction with ex situ electron microscopy, this study evidenced a deep restructuring of the nanoparticles under reaction conditions, which was correlated to their unexpected selectivity for oxygenated products. This work should promote investigations on these advanced nanostructures for selective catalysis.

References:
S. Carenco et al., *Small* 2015, in press.
COLL 383

Probing cooperative phenomena in nanoscale metal catalysts by operando techniques

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Nanometer-size metal particles on high surface area supports have a rich variety of physicochemical properties that attract growing interest across multiple scientific and technological areas. For instance, it has been shown both experimentally and theoretically that catalytic activity, selectivity, and stability of many types of supported metal catalysts depend, among other factors, on their structure, morphology, crystalline order, charge state and interaction with the support. An important recent finding is the cooperative behavior of multiple attributes of a particle-support-adsorbate system. The influences of particle geometry and interactions with the support as well as adsorbates on the catalysts reactivity are shown to be correlated in a complex manner with each other, thus preventing their separate investigations. For example, we demonstrated that the charge state of nanometer-size Pt/γ-Al₂O₃ catalysts is influenced largely by three interactions: between (i) particle and support, (ii) particle and adsorbates, and (iii) adsorbates and support. A combination of theoretical and experimental techniques is needed to resolve multiple competing interactions within these systems, their interactions with environment, as well as their changes under realistic operating conditions. I will describe our efforts to correlate experimental results obtained for nm-scale supported Pt clusters by multiple in situ and operando probes and first principle simulations. We aimed at addressing the following main questions:

1) What is the hierarchy of most important factors that affect the electronic properties of the catalysts?
2) Is the qualitative description of the average atomic arrangements and overall electronic properties of the catalyst sufficient to capture its physicochemical behavior or is more detailed knowledge of intra-particle distributions of atoms and charges needed?
Examples will be shown of the use of high energy resolution methods of X-ray absorption and emission spectroscopies, as well as the situ IR spectroscopy and in situ electron microscopy. Together with first-principle modeling of the data, new information about the heterogeneity of atoms and charges within a representative, supported catalytic particle was obtained.

COLL 384

Structure of carbon supported bimetallic Pt-M catalysts during aqueous phase reforming of biomass derived oxygenates

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Lignocellulosic biomass is a promising renewable resource for the production of fuels and chemicals. Designing more active, and especially more selective catalysts will define the role of catalysis in meeting our energy demand and lowering our dependence on fossil fuels. Catalytic aqueous phase processing of biomass derived sugars is one of the promising renewable routes for the synthesis of fuels and chemicals. However, to enable the design of more active and selective catalysts, it is essential to determine the catalyst structure and its surface chemistry in the condensed phase to correlate the structure with the reaction kinetics.

The talk will cover our recent research efforts in understanding how the condensed phase affects Pt-M/C bimetallic catalysts (M = Re, Co) catalyst structure, surface chemistry and activity/selectivity during aqueous phase reforming of glycerol. The catalysts were probed by \textit{operando} XAFS, \textit{in situ} ATR-IR and Raman spectroscopies. We show that the catalyst surface is strongly affected by the exposure to the reaction conditions which in turn affects the catalyst activity/selectivity. For PtCo/C, reverse Monte Carlo simulations of the \textit{operando} XAFS results show that the nanoparticles undergo restructuring from a Pt@Co core-shell after reduction to a PtCo random alloy upon exposure to the reaction conditions. For PtRe/C, XAFS, ATR-IR and Raman suggest that the reaction conditions result in partial oxidation of Re. The effect of these oxidized Re species on the electronic properties of Pt and on the adsorption and desorption of CO will be presented. In addition, we will discuss how these insights into the surface chemistry can guide the catalyst design for tuning the selectivity towards either H\textsubscript{2} generation or hydrodeoxygenation for the production of fuels.

COLL 385

Isolation of reactive chemical species in heme-containing metal-organic frameworks
This presentation will outline our efforts to isolate, study, and explore the reaction chemistry of reactive chemical species in heme-containing metal-organic frameworks (MOFs). In particular, the chemistry of solids derived from the material PCN-224 with oxygen- and nitrogen-atom transfer agents will be detailed. This work has led to the structural characterization of several species that have proven to be unstable in related molecular complexes, including a five-coordinate oxyheme species. In addition to their structural characterization using single-crystal X-ray diffraction, these compounds have been subjected to an array of spectroscopic and magnetic analysis. For instance, Mössbauer, diffuse reflectance UV-visible, and extended X-ray absorption fine structure spectroscopies, along with variable-temperature dc magnetic susceptibility measurements, have been carried out in order to interrogate the electronic structure and local coordination environment of the isolated species. Finally, the ability of these reactive species to carry out stoichiometric and catalytic group transfer chemistry with substrates such as alkanes and olefins will be discussed.

**COLL 386**

**Multifunction chemical sensors designed on 2D nanomaterials for detection and degradation of low-level contaminants**

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Anchoring of semiconductor and metal nanoparticles on single layers 2-D materials (graphene oxide and molybdenum disulfide) by a solution processable procedure allows the convenience of creating a multifunctional catalyst mat with the ability to both detect and degrade toxins. A photocatalytic activation method has been used to deposit metal nanoparticles on semiconductor / graphene films, resulting in the formation of SERS active surface for detection and reduction of low-level organic contaminants. Manipulation of photoinduced charge transfer processes on a graphene based catalyst mat allows tailoring of the properties for photocatalytic and sensing applications. The role of the graphene is to establish electronic communication between semiconductor and metal nanoparticles while promoting adsorption of molecules near the nanoparticle surface. Further implementation of 2-D single to few layered molybdenum disulfide nanosheets is studied. Environmental remediation can be achieved by employing these multifunction catalyst mats to concentrate, detect, and degrade organic contaminants via photoinduced chemical reactions.

**COLL 387**

**Golden age of colloids and surfaces**
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Gold colloids have been prepared chemically by Faraday in the 1850's, Turkevich in the 1950's, Frens in the 1970's. Until the 1990's, colloidal gold's claim to fame was (i) transmission electron microscopy stain or (ii) dietary supplement (!). But since the advent of nanotechnology research and development in the 1990's until the present, nanoscale noble metal nanoparticles have become an enormous focus on many scientific fronts. These fronts include detailed mechanistic experiments on controlled crystal growth at the nanoscale; nanoscale assembly; optical properties for chemical sensing, biological imaging, and light-to-heat conversion; and unusual optical properties for metamaterials applications. We are indeed in a new "golden age" in colloid and surface science. In this talk I will highlight both the opportunities and challenges in the world of colloidal gold nanoparticles, with emphasis of course on the research from my own group.

COLL 388

Biointerfaces: Beginnings, state-of-the-art, and horizons

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Biointerfaces profoundly impact our lives and technologies – consider medical implants, surface diagnostics, microfluidic devices, drug therapies and biocatalytic processing; on the negative side we can express concern about marine biofouling, dental plaque and doorknob bacterial transmission. In this talk, I'll explore the roots of biointerface thinking starting with medical implants going back more than 3000 years and working forward in time to pioneers like Benjamin Franklin, Agnes Pockels and, of course, Irving Langmuir. But the focus will be on developments originating around World War II that led to contemporary biomaterials, an understanding of proteins at interfaces and life-saving medical implants. The state-of the-art today is characterized by powerful surface analytical tools, flexible strategies for precision surface modification, an enhanced understanding of biocompatibility and accurate surface-based diagnostics. Each of these biointerface contributions will be explored with examples from my own work and from the work of other contemporary leaders. Finally, speculation on the future of the biointerface will be presented by considering where surface instrumentation will go, and how we might create extremely smart surfaces for probing and controlling biology.

COLL 389

Bridging combustion and nanotechnology

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Intersection between combustion and nanotechnology offers exciting opportunities to provide mutual benefits for both areas. This lecture will present several examples of our efforts in bridging combustion and 1-D nanomaterials. First, we developed several flame synthesis methods to synthesize, decorate or dope 1-D metal oxide nanomaterials and these materials exhibit much enhanced photoelectrochemical water splitting performance. Second, we applied 1-D transition metal oxides to catalyze the oxidation reactions of hydrocarbons. These 1-D nanostructured catalysts compared to the supported NPs, exhibit comparable or even better catalytic activity and stability, great flexibility in increasing the catalyst loading, and convenience in tuning the surface chemistry. Finally, we demonstrated a distributed optical ignition method that uses a camera flash to ignite Al NPs, resulting in the ignition of solid phase energetic materials, and liquid and gaseous fuels.

**COLL 390**

**Crystal chemistry at the molecule-substrate and molecule-molecule interface in organic electronic systems**

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Exciting chemistry occurs at organic interfaces. Consider an organic field-effect transistor: charge generation and transport both occur at the organic interface. From a fundamental viewpoint, the role of the interface must have optimal electronic and physical communication in order to yield highly efficient devices. From a technological viewpoint, one must understand, control, and have a rational design of the desired electronic and optical properties at the organic interface for the development of solar cells, integrated circuits, light-emitting transistors, and a host of potential new device concepts that have not yet been realized. In this lecture, I will discuss our efforts in investigating molecular orientation at substrate and organic interfaces. For example, we have synthesized single-crystalline donor-acceptor nanowire devices (i.e. transistors, solar-cells) that have enabled us to demonstrate efficient charge separation and ambipolar charge transport. We have also developed a method for growing oriented single-crystal nanopillars at graphene interfaces for use in high performance organic solar cells. The use of organic single-crystalline devices will have a major impact in accelerating the emerging area of organic electronics, as these highly ordered systems will enable one to extract intrinsic charge carrier transport phenomena that cannot be accurately determined from disordered systems common to amorphous and/or polycrystalline films used in mainstream devices.
Vertically oriented single-crystalline CuPc nanopillars grown on graphene substrates.

**COLL 391**

**Electrostatically assembled protein-polymer nanoparticles for cartilage repair**

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The repair and rescue of damaged cartilage tissue has been a significant challenge, with most traumatic joint injuries progressing to osteoarthritis, often very rapidly. Transport of systemically administered drugs to the cartilage is hindered by the lack of vascularity in the cartilage, and may cause toxicity in other tissues. When drugs are injected in the intra-articular joint space, the dense extracellular matrix (ECM) of the cartilage presents a barrier to the entry of therapeutics, which rapidly diffuse away from the site of administration. This study investigated the use of polymeric nanoparticles to transport therapeutic molecules into the cartilage. We explored nanoscale protein-polymer particles that were sufficiently small, yet stable enough to enter the cartilage matrix and interact with the molecules comprising the ECM. Using electrostatic
complexation, we formulated nanoparticles comprised of complementary charged polypeptides and insulin-like growth factor-1 (IGF-1). By varying the molecular weight and ratio of the component polyelectrolytes, we tuned the size and zeta potential of the resulting nanoparticle between 40 to 250nm and -30mV to +40mV, respectively. The protein component of the nanoparticle varied from 5% to 15% by mass. An in-vitro activity assay revealed that the nanoparticle containing growth factor induced proliferation at levels comparable to native growth factor. Using a rat osteoarthritis model, we monitored the transport and retention of nanoparticles administered via an intra-articular injection in an injured knee joint. In vivo tracking of fluorescently labeled nanoparticles revealed that particles with a net positive charge were retained longer, up to 2 weeks post injection. In contrast, naked IGF-1 alone was rapidly cleared within a few days after administration. Confocal imaging of the explanted cartilage tissue revealed an inverse correlation was observed between the size and the number of particles retained in the cartilage. Co-localization of the particles was observed with (densely) negatively charged ECM molecules such as aggrecan. Histology revealed that cartilage damage was delayed or prevented altogether by the administration of a single dose of nanoparticles within 48 hours of the injury. The matched dose of naked IGF-1, in contrast, was not sufficient to prevent cartilage damage. This study indicates the possibility of using protein-polymeric nanoparticles with regenerative properties for cartilage repair.

COLL 392

Exploring the synthesis, structure, and biological activity of concatenated siRNA polymers

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siRNA is being evaluated as a potential therapy for a number of diseases including cancer and different strategies are being investigated to assemble siRNA into higher order structures to effect its delivery and influence its activity. We have been exploring the synthesis and biological activity of concatenated siRNA molecules; periodic siRNA polymers formed through a rolling circle transcription reaction. These high molecular weight RNA molecules can induce potent gene silencing in addition to possessing other interesting biological activity. We have found that the sequences and secondary structures of the DNA templates used in the rolling circle reaction have a profound impact on the size and yield of csiRNA produced. These studies enabled us to optimize the reaction conditions for synthesizing csiRNA and tune its structure, processing, and activity. In addition to triggering RNAi, we found that csiRNA is a potent inducer of cell death in a variety of cancer cell lines. Finally, csiRNA shows unique assembly with cationic polymers compared with monomeric siRNA. This leads to improved polyplex
stability in certain instances relative to monomeric siRNA, which can significantly increase blood circulation half-life in mice.

**COLL 393**

**Application of polysaccharide-based stabilizers in batch and microfluidic emulsification for preparing polylactide particles with drug delivery applications**

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Polysaccharide-covered polyester particles were prepared by two procedures: emulsion/solvent evaporation in batch¹² and emulsion/solvent diffusion in microfluidics³. The core of particles was made of polylactic acid (PLA) while their surface was covered by dextran chains via the use of water-soluble randomly hydrophobized dextran (Fig. 1) as a polymeric stabilizer.

**Figure 1.**

We demonstrated that hydrophobized dextrans acted as efficient stabilizers in both processes, limiting aggregates formation. Process conditions were varied in order to obtain nano- and microparticles covering a wide range of diameters (between 0.1 and 500 µm) with reproducible and narrow size distributions. Encapsulation and release of polyphenolic molecules (PM, undisclosed substances) were examined with a focus on the effects of fabrication process and PM structure (alkyl group R, Fig. 1). The miscibility of PM with PLA in solid state was characterized by modulated differential scanning calorimetry. The more hydrophobic the PM, the lower its miscibility with PLA was. On the contrary, encapsulation was strongly increased in the case of more hydrophobic PM. Loaded particles elaborated by both processes were characterized and compared regarding their size distribution, surface coverage, and thickness of polysaccharide superficial layer. We demonstrated that the use of dextran-based stabilizers ensured colloidal stability over a wide range of ionic strength (up to 4 mol/L NaCl) and allowed re-dispersion after freeze-drying. More precisely, the structure of dextran-based stabilizer appeared as an important parameter, particularly the number of attached hydrophobic groups (Fig. 1).

**References**

Photocrosslinked polymersomes as responsive and multifunctional synthetic bionanoreactors

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Robust, multi-responsive and multifunctional nanovesicles are in high demand not only as cutting edge drug delivery systems and in synthetic biology, but also for application in microsystem devices and in nanotechnology. Here, responsive nanoparticles based on photocrosslinked polymersomes will be introduced. While pH sensitive polymersomes usually disassemble upon acidification, ours show a definite swelling, since the cross-linked membrane remains intact and allow pH-dependent diffusion of small molecules through the membrane. Thus, cascade enzyme reactions could be carried out under pH control using polymersome-encapsulated enzymes in a one-pot arrangement. In addition, by coassembly of specifically end-functionalized block copolymers and making use of efficient post-functionalization, heterofunctionalization of the polymersomes on their surface is possible. Thus targeting groups could be introduced into the polymersome membrane which allows using our pH-responsive polymersomes for specific cell targeting and pH induced drug release. Furthermore, multifunctional, pH-responsive and photo-crosslinked polymersomes decorated with adamantane and azide groups have been prepared and were used for the subsequent post-modification of the polymersome surface by using covalent and non-covalent approaches. Thus nitroveratryloxycarbonyl protected amine (NVOC) molecules as
photoactive moieties have been introduced through azide-alkyne click reaction to provide light controllable surface functionalization with amines. The non-covalent approach was carried out subsequently to introduce further moieties making use of the strong adamantane-cyclodextrin host-guest interaction processes. Overall, the tunable membrane permeability combined with the potential for introducing light-induced as well as specific non-covalent conjugation sites make these smart polymersomes promising nanocontainers for many applications.

Nanocapillary binding of particles: A generic approach for assembling reconfigurable structures at nanoscale

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Capillary forces operate when any two surfaces interact via a fluid interface. These forces are responsible for various naturally occurring phenomenon such as adhesion of insect to surfaces, sandcastle formation, and mineral sintering. Recently, we reported that nanocapillary lipid binding between maghemite nanoparticles (γ-Fe₂O₃) can form a new class of nanoparticle-lipid microfilaments with unprecedented flexibility and self-healing properties. In the presence of uniform magnetic field, the magnetophoretic attraction of the particles combined with interparticle dipole-dipole attraction drives the microfilament assembly. The fluid like lipid layer on the particles leads to the surface stickiness of the filaments and the magnetic field concentration overcomes the potential electrostatic repulsion in the water phase. The lipid capillary bridges formed between the particles facilitate their permanent binding and sustain the flexible microfilament
structure. The generic nature of this nanoparticle binding approach has now been demonstrated by extending it to non-magnetic silica surfaces. Amine functionalized silica nanoparticles form surface condensed lipid layer which further results into the formation of diffusion limited fractal nanoaggregates. We use Small Angle X-ray Scattering (SAXS) to further investigate the bridging process and the role of lipid in nanocapillary binding of the particles. We analyze the SAXS profiles on the basis of spherical particles interacting via square-well attractive potential. We further demonstrate that this fluid induced nanoparticle binding can be used to formulate aqueous dispersions and gels with unusual rheological and mechanical properties.

**COLL 396**

**Repeat-protein hierarchical self-assembly results in hierarchical and anisotropic mechanical properties**

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Complex hierarchical structures provide beneficial structure-property relationships that can be exploited for a variety of applications in engineering and biomedical fields. Here we report on molecular organization and resulting mechanical properties of self-assembled designed repeat-protein films. Self-assembly of the designed 18-repeat consensus tetra-tripeptide repeat protein (CTPR18) is driven by the combination of head-to-tail stacking and weak dipole-dipole interactions. Wide-angle x-ray diffraction indicates orients normal to the casting surface while small-angle measurements and electron microscopy show a through-plane transversely aligned laminar sheet-like morphology. We will further highlight the effect that this hierarchical structure has on the material’s mechanical properties. We have used nanoindentation and dynamic mechanical analysis to test the mechanical properties over multiple length scales, from the molecular level to the bulk. The morphology of self-assembled material predictably affects the film’s mechanics from the nano- to the macro-scale, with the axial modulus values ranging from 2-5 GPa. The predictable nature of the structure-property relationship of CTPR proteins and their assemblies proves them a promising platform for material engineering.

**COLL 397**

**Development of agent-detecting nanofiber sensors for garments**

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The goal of this project is to develop nanofiber sensors that can be tuned to respond to targeted classes of chemicals, including toxic industrial chemicals (TICs) and organophosphates. These nanofiber sensors could potentially be incorporated into
fabrics, enabling low-burden (e.g., weight, power, size) chemical threat detection in garments. This paper presents our recent progress in developing a prototype wearable sensor composed of novel electrospun polymer and carbon composite nanofiber sensing material with portable low-cost electronics. In this sensor, the composite polymer nanofibers form chemo-resistor-sensing materials because the conductivity changes in proportion to concentration when exposed to chemical vapor. In this study, the composite polymer nanofiber material was demonstrated to be sensitive to sub-ppm levels of agent simulant vapors, such as dimethyl methylphosphonate (DMMP), a nerve agent simulant; 2-chloroethyl ethyl sulfide (CEES), a blister agent simulant; and methyl salicylate (MeS), used in the Man-in-Simulant Test (MIST) of protective garments. Furthermore, this nanofiber-based sensor was demonstrated to be able to not only detect chemicals in the vapor phase, but also droplets of these analytes by diffusing vapor from the droplet through a protective hydrophobic membrane. The sensor was found to be rugged enough to survive simple rubbing and tapping tests without degrading sensor performance. The sensitivity and selectivity of this sensor to different vapor analytes and the interference of temperature and humidity changes will also be discussed. These results have important implications for designing agent-detecting wearable sensors for garments.

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COLL 398

Hybrid graphene oxide for trace level identification of explosives selectively using Raman fingerprint

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Trace level identification of explosive molecules are very important not only for security screening but also for the environment and human health. Here we will discuss our recent reports on gold nanoparticle-graphene oxide hybrid platform for the spectral fingerprint and the trace level identification of RDX and TNT. Reported data indicate that the surface enhanced Raman spectroscopy (SERS) enhancement factor for graphene oxide (GO) attached gold nanoparticle assembly is four orders of magnitude higher than only nanoparticle. We have demonstrated that label-free nitro-explosive identification limits using hybrid platform can be as low as 10 femto molar (fM) for TNT and 500 fM for RDX.

COLL 399
Sensing, decontamination, and filtration by the multifunctional zirconium hydroxide

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As the threat of chemical warfare agents and toxic industrial chemicals persists throughout the world, materials development for protection against these threats continues to be of utmost importance. Indeed, a wide variety of nanostructured sorbents have been studied over the last decade in attempts to develop highly active structures targeting both broad spectrum protection and highly specific chemistries.

In this talk, we will discuss the development and use of zirconium hydroxide based materials for a wide range of chemical defense applications. By itself, the amphoteric surface created from a combination of bridging and terminal hydroxide groups provides substantial reactivity toward nerve agents such as soman and VX, and is currently being investigated for enhanced decontamination technologies. Adding co-precipitated metals to the substrate, such as zinc, cobalt, and silver, produces a highly active material for the filtration of acidic/acid-forming gases. Finally, changes in surface chemistry due to adsorption of various toxic gases allows for use of zirconium hydroxide in sensing applications. Adding dyes to the structure further enhances sensing capabilities.

COLL 400

Novel nanostructured colorimetric sensor for the detection of explosives

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A compact, highly responsive, novel nanostructured colorimetric sensor for the rapid detection of explosives was developed. The sensor allows colorimetric explosive detection by the naked eye analogous to the red, yellow, green traffic signals, facilitating ease-of-use and fast, efficient response. Electrospun nanofiberous polymers conjugated with tetrathiafulvalene (TTF)-based colorimetric dyes was developed for the highly sensitive detection of ultra-trace nitroaromatic explosives (2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT), cyclotetramethylenetetranitramine (HMX), 3,5-trinitroperhydro-1,3,5-triazine (RDX) and pentaerythritol tetranitrate (PETN)), where the latter two are main components of highly energetic plastic explosives, such as C-4 (91% RDX) and Semtex (40–76% PETN). The TTF-based dyes are capable of changing their physiochemical properties when exposed to the explosives. We hypothesize that these TTF-based dyes form charge-transfer complexes with the electron-deficient guests i.e. DNT, TNT Tetryl, HMX, PETN and RDX. Such aromatic complexes give easy-to-visualize color changes when the dyes have selectively interacted with the explosives in organic solution and in the vapor phase. The color changes were also be quantified using a tri-stimulus calorimeter. When the dyes are immobilized on the nanofiber
surface, significant enhancement or amplification of the color changes was obtained allowing parts-per-trillion level detection of the explosives in the vapor phase. The extremely large surface area of the nanofibers also facilitated visual color detection by the naked eye. The advantages of this colorimetric sensor system are that it is inexpensive, requiring very small amounts of dyes and no complicated analytical instrumentation for detection, and can be potentially be employed as a single-use disposable. Another advantage of dye-based sensors is that they do not require a separate reference sensor. This work paves the way to design a portable sensing device using low-cost fabrication and detection methods. Such a sensor technology could be applied in airports, in law enforcement, and military applications where fast, efficient screening for explosives are necessary.

**COLL 401**

**Detection of biological threats using gold nanoparticles in lateral flow immunoassays: Dengue hemorrhagic fever**

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Viral hemorrhagic fever viruses populate the category A of NIAID biodefense agents list, due to their high transmissibility and cause of high mortality. Dengue, in particular, is a mosquito-borne tropical disease that has caused major epidemics and hospitalization in endemic areas during the last decades. Accurate diagnosis of dengue fever is critical to treat individual patients and to predict epidemics. Lateral flow devices are ideal candidates to diagnose diseases in remote areas because they can be operated by non-experts, are cheap, portable, and do not require electric power to be operated. We present results on a machine-readable multiplexed lateral flow device for the detection of several tropical disease markers. By making the device readable by a mobile phone, it is able to provide real-time epidemiologic data to monitor disease distribution based on diagnostic data. The device relies on a lateral flow immunoassay, which uses capillary flow and the accumulation of ligand-coated nanoparticles to detect the presence of target proteins. Gold nanoparticle-antibody conjugates are critical to ensure that the device will have enough sensitivity to detect the illness even at low concentrations of target protein, such as in early stages of the disease. The sensitivity of lateral flow devices greatly depends on the nature of the ligand-target pair and their binding thermodynamics on the nanoparticle interface. We engineer the nanoparticle shape, size, surface chemistry, and biofunctionalization in order to lower the overall detection limit of the device. The nanoparticle surface properties and biofunctionalization are characterized by gel electrophoresis, DLS, and fluorescence/optical spectroscopy in conjunction with chemical displacement. These new, effective, low-cost devices would be very useful in developing countries, but also for developed countries, where they can contribute to lowering the overall cost of healthcare and enable widespread use for other applications such as crowdsourcing.
Multicolored silver nanoparticles for multiplexed disease diagnostics: Distinguishing dengue, Yellow Fever, and Ebola viruses

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Rapid point-of-care (POC) diagnostic devices are needed for field-forward screening of severe acute systemic febrile illnesses. Multiplexed rapid lateral flow diagnostics have the potential to distinguish among multiple pathogens, thereby facilitating diagnosis and improving patient care. Here, we present a platform for multiplexed pathogen detection using multi-colored prism-shaped silver nanoparticles (AgNPs). We exploit the size-dependent optical properties of Ag NPs to construct a multiplexed paperfluidic lateral flow POC sensor. AgNPs of different sizes were conjugated to antibodies that bind to specific biomarkers. Red AgNPs were conjugated to antibodies that could recognize the glycoprotein for Ebola virus, green AgNPs to those that could recognize nonstructural protein 1 for dengue virus, and orange AgNPs for non structural protein 1 for yellow fever virus. Presence of each of the biomarkers resulted in a different colored band on the test line in the lateral flow test. Thus, we were able to use NP color to distinguish among three pathogens that cause a febrile illness. Because positive test lines can be imaged by eye or a mobile phone camera, the approach is adaptable to low-resource, widely deployable settings. This design requires no external excitation source and permits multiplexed analysis in a single channel, facilitating integration and manufacturing.
COLL 403

Sensing and imaging with isotropic and anisotropic metallic nanostructures

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In this talk, we will describe recent advances in chemical analyte detection and optical imaging applications using anisotropic metallic nanoparticles. Noble metal nanoparticles, particularly gold and silver, have exciting physical and chemical properties that are entirely different from the bulk. For chemical sensing and imaging, the optical properties of metallic nanoparticles provide a wide range of opportunities, all of which ultimately arise from the collective oscillations of conduction band electrons ("plasmons") in response to external electromagnetic radiation. Several optical sensing and imaging modalities for metallic nanoparticles will be covered: (1) aggregation dependent shifts in plasmon frequency; (2) local refractive index-dependent shifts in plasmon frequency; and (3) inelastic (surface-enhanced Raman) light scattering. The surface chemistry of the nanoparticles must be tunable to create chemical specificity for signatures of interest, and is a key requirement for successful sensing and imaging platforms.

COLL 404

Self-assembled peptide amphiphile nanoparticles for rational combination therapies against metastatic solid tumors
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Most lung and ovarian cancer patients present with metastatic disease and, despite great advances in the molecular profiling of these tumors, survival rates have only marginally improved over the past decade. A majority of these patients display tumors lacking functional p53, a tumor suppressor protein that mediates cellular response to DNA-damaging chemotherapy. Therapeutic interventions that block p53-independent DNA damage response could, thus, sensitize metastatic lung and ovarian tumors to frontline chemotherapy. RNA interference (RNAi) is one such intervention; however, drugging metastatic tumors with small interfering RNA (siRNA) via traditional pharmaceutical excipients and drug carriers can be challenging. Self-assembled polymer nanotechnologies represent a powerful tool in which tumor-specific cellular delivery of siRNA can be rationally designed and chemically tailored. Recently, we identified a downstream signal effector of the p38 MAPK signaling pathway, the kinase MK2, as a critical component of the DNA damage response in p53-deficient cells. Through the use of a novel family of self-assembling, synthetic peptide amphiphiles nanoparticles, we were able to sensitize lung and ovarian tumor cells to frontline platinum and taxane therapy in vitro and deliver mRNA-depleting siRNA to metastatic lung and ovarian tumor models in vivo. siMK2 therapy sensitized metastases to frontline chemotherapy, decreasing subsequent tumor burden and improving overall survival. Peptide amphiphile-based RNAi against MK2 could serve as a powerful tool to improve frontline lung and ovarian cancer chemotherapy in the clinic.

COLL 405

Functionalization of single walled carbon nanohorns for simultaneous fluorescence imaging and cisplatin delivery

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Bladder cancer continues to plague more than 50,000 new patients each year, resulting in more than 10,000 deaths, invasive surgeries, and chemotherapy. Complete resection of the bladder is the most common form of treatment, but patients undergoing these procedures have a significantly decreased quality of life following surgery. New strategies for treating these cancers efficiently and effectively are needed to improve the quality of life of these cancer patients. Single walled carbon nanohorns (SWNHs) serve as both photothermal and drug delivery agents for bladder cancer therapy, showing significant tissue heating following near infrared irradiation in vivo. The potential for
SWNHs to function as a nanotheranostic vehicle with the capability for both chemotherapeutic delivery and dynamic imaging is investigated through simultaneous delivery of the chemotherapeutic cisplatin from SWNH cone interiors and imaging of nanoparticle transport using quantum dots (QDs) conjugated to SWNH surfaces (Figure 1a,b). Following successful formation of SWNH-QD + cisplatin conjugates, drug release profiles show that the addition of QDs does not hinder the cisplatin delivery capabilities of SWNHs. These results are confirmed with cytotoxicity measurements of in vitro cultures of AY-27 rat bladder carcinoma cells. In addition, the conjugates were effective imaging beacons over the course of 3 days in cell culture, revealing that endocytosed SWNHs continue to deliver therapy after removal of the nanoparticle solution (Figure 1c). The capability to monitor transport of this therapeutic SWNH conjugate will ultimately enable the optimization of nanoparticle properties and its delivery method to achieve maximum therapeutic efficacy.

Figure 1. a) Schematic of SWNH-QD + cis, b) TEM image showing the presence of QDs on SWNH surface and cisplatin within SWNH cones, c) Fluorescent image of AY-27 rat bladder cancer cells incubated with SWNH-QD + cis for 48 hours. Green = F-actin, Blue = Nuclei, Red = QD.

COLL 406

Etchable plasmonic and quantum dot probes to image and quantify cellular internalization in vivo

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Understanding the internalization of nanoparticles into cells is critical for the coming wave of genetic and drug delivery vehicles. Nanoparticle-based fluorescence imaging does not usually allow cell membrane-bound particles and intracellular particles to be distinguished from each other. We show that by using functionalized nanoparticles as probes, this distinction can be made following a rapid, non-toxic etching process that selectively removes the extracellular nanoparticles but leaves the intracellular nanoparticles unharmed. Two material systems are described along with novel examples of in vivo chemistry – one strategy using silver plasmonic cores and the other using semiconductor core/shell quantum dot nanoparticles (CdSe/ZnS). The silver nanoparticle (AgNP) etching is based on the sensitivity of Ag to a biocompatible redox-buffer solution based on hexacyanoferrate and thiosulfate. We demonstrate that after injection of peptide-functionalised nanoparticles into blood circulation and their receptor-based tumor homing, injection of etchant (in the live animal) removes signals coming from nanoparticles or quantum dots that are outside of cells anywhere in the body, leaving the internalized pool for imaging and quantification. The fraction of nanoparticles inside cells in the tumor was found to increase with the etching delay time, thus revealing the internalization kinetics and enabling new parametric comparisons between targeted nanoprobes. Disassembling nanosystems such as these may also reduce side effects and toxicity to off-target organs.

COLL 407

Rapid and quantitative multiplexed nanoparticle platform for the identification by surface-enhanced Raman spectroscopy of cells at low concentrations flowing in a microfluidic channel

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The reliable and fast identification of different types of cells is of utmost importance in several biomedical applications. The detection of cancer cells in bio-fluids such as urine and blood could be crucial to detect patient response to therapy, to monitor drug resistance effects, as well as for early identification of disease recurrence, and ultimately for a personalized medicine approach. Fast detection of bacteria in the blood is a fundamental requisite for higher chances of survival during septic events. We developed bright, spectrally rich, multiplexing SERS Biotags (SBTs), composed of a silver nanoparticle dimer core. The SERS spectrum of an individual SBT acts as a unique barcode that is easily differentiable in a composite SERS spectrum originating from many tags. The SERS intensities achieved are comparable to fluorescence and can all be excited with one laser. SBTs can label cells using antibodies, aptamers and peptides. We have now developed a platform that combines a microfluidic chip with
SBTs for the identification of individual cells on the fly. In a flow-focused microfluidic channel we injected either (i) a mixture of cancer and normal cells, or (ii) polystyrene beads as cell-proxies, all pre-labeled with SBTs. We demonstrate the identification of individual cells or cell proxies by spectral unmixing of the Raman signature of each SBT-labeled cell passing single-file through the Raman laser. To do so, we developed a qualitative categorization algorithm based on principal component analysis, and a quantitative model based on classical least squares. In summary, we demonstrate the rapid multiplexed identification cancer cells at low concentration, or beads with up to four SBTs simultaneously.

Cancer and normal cells, prelabeled with a cocktail of cancer-specific and control SBTs (the latter binding both cell types), are injected into the device, where they are flow-focused before passing through the Raman laser. The SERS spectral signature for each cell is recorded and analyzed by the PCA and CLS models to identify whether it is cancerous or normal.

COLL 408

Nanoscience approach to the synthesis of novel radionuclide substrates

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We have synthesized and characterized the first example of an atomically precise 2-D film of radioactive atoms. Our data indicate that radioactive iodine-125 (I-125) atoms form well-ordered monolayers on gold/mica substrates that are stable under ambient
conditions and amenable to study by high resolution microscopy and surface analysis techniques. We observe nuclear transmutation of I-125 to Te-125 at the individual atom level and support our elemental assignments with theory. The reduced dimensionality of these surface-bound films provides the ability to study the microscopic details of radiation chemistry, biological degradation and material damage induced by high-energy nuclear processes. Most significantly, our results indicate that interaction of I-125 with metallic surfaces produces more than 5x the expected flux of extremely reactive electrons that accompany the high-energy gamma/X-ray emission and are peaked in the 0–20 eV range. These lower energy electrons are the most important species in radiation induced chemistry and biological damage due to their efficiency for breaking chemical bonds and their sub-cellular range. Interest in tunable low-energy electron sources was sparked by work showing this can be accomplished in multi-atom systems with covalent bonding, yet no practical examples have been realized. Our discovery has great promise as I-125 is commonly used in medical imaging, radiation therapy and biological assays and the I-Au surface chemistry described here is transferable to biocompatible gold nanoparticles.

Overview of radioactive $^{125}$I monolayer film preparation and characterization
Stimuli-responsive reagents for improved cell isolations


An efficient and cost-effective cell isolation process is critical to the broad application of chimeric antigen receptor T cell (CART) therapy and circulating tumor cell (CTC) diagnostics. CART adoptive immunotherapy has shown great promise in clinical trials for cancer treatment, but the manufacturing process is complex, specifically with respect to achieving rapid and efficient isolation of T cells from patient blood. In patients with metastatic cancer, CTC identification and enumeration have been used as markers of tumor burden, metastasis, tumor recurrence and survival. Although there is a FDA-cleared CTC kit (CellSearch®), the isolation of rare and heterogeneous CTCs with high purity and yield for downstream analysis remains a challenge. Thus, Nexgenia is developing stimuli-responsive polymer-based systems that are aimed at improving cell isolations for immunotherapy and CTC diagnostics. The stimuli-responsive polymers are synthesized via reversible addition fragmentation chain transfer (RAFT) techniques and engineered to respond to changes in temperature. Nexgenia’s binary reagent system is comprised of cell-targeted antibodies conjugated to stimuli-responsive polymers and magnetic nanoparticles (mNPs) incorporating similar polymers. After incubations with cells, a stimulus (temperature shift) quickly induces aggregation of polymer-coated mNPs with the cell-bound polymer-conjugated antibodies, thus allowing rapid isolation of cells with simple magnets. Reversing the stimulus solubilizes the mNPs and antibody conjugates so that mNPs can be removed from cells before further processing, unlike most other magnetic bead-based isolation technologies. Here, two binary reagent systems are developed with aggregation temperatures of either ~30°C or ~15°C. These systems are used to enrich different T cell subsets (e.g., CD4) from human peripheral blood mononuclear cells with similar performance and speed as a commercial (Miltenyi Biotec) system. The rapid and efficient isolation of target cells, combined with easy mNP removal after cell isolation, are exciting properties to exploit in further development of cell therapy and diagnostic reagent kits.

COLL 410

Theranostic graphene quantum dots decorated magnetic nanoparticle for selective capture and two photon imaging of rare tumor cells in second biological window

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Hepatocellular carcinoma is the third leading cause of cancer-related deaths. Now it is well documented that circulating tumor cells (CTCs) in blood can be used as a biomarker for early stage detection of liver cancer. Since CTCs are extremely rare malignant cells in blood containing billions of other cells, till now it is a huge challenge to capturing and identifying CTCs with sufficient sensitivity and specificity. Here we will...
discuss our recent reports on the development of multifunctional biocompatible graphene oxide quantum dots (GOQDs) coated high luminescence multifunctional magnetic nanoparticles for selective separation and diagnosis of liver cancer tumor CTCs from infected blood. Our reported data indicate that anti-GPC3 antibody attached multifunctional nanoparticle can be used for selective Hep G2 HCC tumor cell separation and enrichment from infected blood samples even in the 10 cells/mL blood level. We have also shown that anti-GPC3 antibody attached GOQDs coated magnetic nanoparticle can be used as a two-photon luminescence platform for selective and very bright imaging of Hep G2 tumor cell in the biological transparency window using 960 nm light.

**COLL 411**

**Engineering remotely triggered liposomes to target triple-negative breast cancer**

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There is still no clinically approved, targeted treatment option for Triple-Negative Breast Cancer (TNBC). Many chemotherapy drugs approved for the treatment of cancer are poorly water-soluble and are administered unmediated to the body, resulting in limited effectiveness and increased toxicity. Liposomes, an engineered biological nanoconstruct clinically approved for the treatment of cancer, address drug solubility issues by encapsulating both hydrophobic and hydrophilic drugs. Polyethylene glycol (PEG) covalently bonded to the liposomes potentially lowers the immune reaction of the nanoconstruct in vivo. Drug loaded liposomes modified with ligands to specifically target cancerous cell receptors may reduce damage to healthy tissue. Verteporfin (BPD), a hydrophobic, non-toxic photosensitive drug, may be used for fluorescence-based imaging and reactive oxygen mediated cytotoxic therapy. Photodynamic therapy (PDT) triggers BPD through 690 nm light irradiation. Online image-guided PDT with targeted BPD-loaded liposomes would be an attractive nanotheranostic for TNBC.

This study will observe the toxicity of BPD delivered unmediated and mediated through passive and folate-targeted PEGylated BPD-loaded liposomes before and after PDT in monolayer cultures with breast cancer (MDA-MB-231) cells and co-culture cancerous and normal (MCF-12a) cell lines in vitro. The liposomes will be characterized by size, zeta potential, and drug encapsulation efficiency. Targeting effectiveness will be observed through folate competition tests, fluorescence imaging, MTT assay, and co-culture experiments. Results from this study will be presented.

If successful, this study could form the basis for novel nanoparticle-mediated, targeted PDT of TNBC in the clinic. Future studies can compare liposomes loaded with multiple
drugs and in 3-D cultures. Similar encapsulation and targeting procedures may be applied to other drugs and cancers.

1,2-Distearoyl-sn-Glycero-3-Phosphocholine (DSPC), Cholesterol (ovine wool) (>98%), 1,2-Distearoyl-sn-Glycero-3-Phosphoethanolamine –N-[Methoxy(Polyethyleneglycol)-5000] (DPSE-PEG), Verteporfin (BPD)

Nitrogen gas powered extrusion of multi-lamellar vesicle, 0.1 μm membrane

Small uni-lamellar vesicle, average 100 nm liposome, encapsulating the hydrophobic photosensitizer BPD

Non-Targeted BPD-loaded Liposomes and Folate-Targeted BPD-loaded Liposomes (A-B). Philips 400 Microscope

MDA-MB-231 cells with Folate-Targeted BPD-Loaded Liposomes 24 hours after Photodynamic Therapy, Light Dose 5 J/cm². Power Settings 200-220 mW, Concentration of Photosensitizer 500 nM

MDA-MB-231 cells with Folate-Targeted BPD-Loaded Liposomes 24 hours after PDT, Light Dose 2.5 J/cm², Power Settings 200-220 mW, Concentration of Photosensitizer 500 nM Fluorescence Key Pseudo Colors: Green – Alive; Red – Dead
Next generation magnetic lipid nanohybrids for theranostics

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Bio-imageable nanoscale assemblies that can be activated and controlled through external stimuli represent the next generation multifunctional theranostics (therapeutics + diagnostics). MRI contrast agents such as iron oxide nanoparticles, which generate thermal energy by an external alternating magnetic field (AMF) or NIR laser, can be effectively used to induce localized hyperthermia or heat-triggered drug release when co-encapsulated with drugs in the lipid nanoparticles (LNP). We have developed well-defined, reproducible, easy to scale up, and size controllable (from 30 nm to 125 nm) hybrid LNP systems that consist of either hydrophobic or hydrophilic magnetic iron oxide nanoparticles encapsulated in various lipid components. We herein present their synthesis and biophysical characterization, as well as their effects in in vitro/in vivo MRI imaging and heat-induced drug release.

Enzyme-instructed self-assembly (EISA) for potential cancer therapy

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The ultimate goal of cancer therapy is to kill cancer cells without harming normal cell. Currently, chemotherapy (e.g., cisplatin) still lacks of selectivity, and molecular therapy (e.g., kinase inhibitors) has limited efficacy due to multidrug-resistant (MDR) originated from the great complexity of cancer, such as tumor microenvironment and intratumoral heterogeneity. These challenges require a paradigm-shift for developing an all-encompassing process that disrupts tumor microenvironment and selectively inhibits cancer cells. Here, we report that enzyme-instructed self-assembly (i.e., the integration of enzymatic transformation and self-assembly) of small peptides results in pericellular molecular fibrils to disrupt tumor microenvironment, interrupt multiple cellular processes, and inhibit MDR cancer cells selectively. Our results show that overexpressed ectophosphatases, as a generic yet currently “undruggable” difference between cancer and normal cells, catalyze the conversion of precursors to self-assembling peptides that form nanoscale fibrils on the cancer cells. These fibrils act as a multifaceted signal to activate multiple death receptors, to block cellular mass exchange, to hinder cell migration, thus inhibiting cancer cells selectively in the co-culture of MDR cancer cells (e.g., MES-SA/Dx5, T98G, and A2780cis) and stromal cells (e.g., HS-5). Besides boosting the activity of cisplatin against A2780cis, the peritumoral administration of the
precursors of the fibrils inhibits tumor progression in a murine model of a drug-resistant cancer (MES-SA/Dx5).

The overlaid confocal images of low (top) or high (bottom) magnification of the cells. Control: cells in DMEM, for 48 h; Treated: cells in DMEM containing 1a (217 μg/mL) for 48h.

**COLL 414**

**EELS imaging analysis of silicon cluster superlattices**

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Three-dimensional superlattice structure of silicon nanocrystals (or silicon clusters in the gas phase) is characterized by collective electronic phenomena, which result from interactions between neighboring nanocrystals. As the distance between adjacent silicon nanocrystals could be reduced in close vicinity to each other below 0.4 nm, silicon nanocrystal superlattices may form covalent valence bonds between nanocrystals; crystallographic coalescence of silicon nanocrystals may occur. Direct
deposition of ligand-free pure silicon clusters in gas phase has generated the silicon cluster superlattice on a graphene substrate with a highly condensed pulsed silicon cluster beam with a monodisperse size distribution.\(^1\) High resolution transmission electron microscopy analysis revealed new characteristics: silicon clusters form body center cubic (bcc) superlattice structures with a lattice constant of 2.134 ± 0.002 nm. Adjacent silicon clusters possess the sp\(^3\) diamond structure with the same lattice constant as monocrystalline silicon. Theoretical investigation, based on the density functional theory, revealed that the adjacent silicon clusters form covalent bonds between Si atoms on the cluster surface with possessing silicon atoms -Si- in common; crystallographic rearrangement of Si atoms on the cluster surface occurs to coalesce into superlattices.\(^2\) Figure 1 shows EELS imaging spectra at 60 keV of the silicon cluster superlattice. The \(L_{2,3}\) edge onset at 99.8 eV, the energy loss indicating transition from the 2p core state to the unoccupied electronic states (UDOS) formed in monocrystalline silicon, demonstrates that the silicon cluster superlattice possesses the same UDOS. We discuss the \(L_{2,3}\) loss peaks at lower energies than 99.8 eV, presenting the electronic states proper to the silicon cluster superlattice.


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**COLL 415**

**Advances in nanomaterial analysis using laboratory X-ray diffraction equipment**

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X-ray diffraction is a relatively common method of physical characterization that is routinely used to study crystalline materials for purposes of “finger-printing” or phase identification. Modern laboratory X-ray diffractometers have grown in capability beyond simply being used for identification purposes, and now are capable of applications such as small angle x-ray scattering (SAXS), which is a technique used to determine the average particle shape and size of nanomaterials.

In this paper we present some recent advances in the x-ray analysis of nanomaterials. Using a PANalytical Empyrean Diffractometer, both wide angle x-ray scattering (WAXS) and SAXS measurements were completed on various nanomaterials such as micelles, colloids, polymers and metal nanoparticles. Measurements were completed using the PANalytical sample stage, the ScatterX78, and an area detector, the PIXcel3D, which provides the ability to study both isotropic and anistotropic materials in 2D. The results presented here demonstrate that high quality SAXS data, that is typically obtained using a stand-alone SAXS instrument or synchrotron source, can also be collected in the laboratory with comparable quality.

COLL 416

Fluorescence lifetime spectroscopy: A new addition to the toolkit used to monitor the formation and degradation of semiconductor quantum dots in solution

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II-VI semiconductor quantum dots (QD) have been used extensively as an alternative to molecular fluorophores in biological assays. Much work has focused on optimizing their photo-physical properties through the development of synthesis protocols that yield QD with broad absorbance, narrow emission peaks, high photo-stability, and size-dependent emission. Core-shell QD were found to be particularly effective because of their increased chemical stability and enhanced photo-physical properties. While the synthesis methods to form core-shell QD are well established, they still often lead to inconsistency in QD structure and properties. In general, the field of nanomaterial synthesis lacks in-situ real time measurement methods to assess nanoparticle quality in the same manner that NMR or IR spectroscopy are used to monitor the progression of organic chemical reactions. To date, steady-state fluorescence spectroscopy, UV-VIS absorbance spectroscopy and transmission electron microscopy are the standard methods employed for the characterization and determination of the overall quality of luminescent QD. Electron microscopy cannot be used for real time monitoring of chemical reactions, and the concentration dependence of steady state fluorescence, and UV-VIS absorbance spectroscopy precludes their use for real time assessment of QD quality because changes in intensity could be the result of variation in QD concentration, and not QD quality. In this study, we employ for the first time, fluorescence lifetime spectroscopy, a non-concentration dependent technique, to provide valuable information about QD core-shell structure as it is formed during synthesis, and as it is degraded in aqueous solutions of increasing complexity. We aim to elucidate the relationships between the fluorescence lifetime of QD and their
properties including surface defects, electron leakage, the core/shell interface, and poly-
dispersity in solution. This presentation will describe the findings of in situ fluorescence
lifetime measurements of QD formed under varying synthesis conditions, as well as,
controlled degradation experiments.

COLL 417

Study nanomaterials using synchrotron X-ray scattering for structures and
kinetics

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Synchrotron based X-ray scattering can measure structural lengths covering form a few
Angstroms to a few hundred nanometers, and has become a very powerful structural
tool for nanomaterial study. For nanomaterials with high homogeneity, this technique
can provide definite structural information on particle morphology and lattice packing. Its
application will be demonstrated in the structural characterization for several peptide
self-assemblies, including nanotubes and nanosheets. In recent years, owing to its non-
destructive nature and high flux, synchrotron based X-ray scattering has been used to
study the kinetics and mechanism of the nanomaterial growth. The oxidation process of
iron nanoparticle has been studied using in-situ x-ray scattering, monitoring particle
morphological change, including the evolution of void spaces within the particle (Figure
1), which cannot be easily studied with other techniques, such as TEM. In the
presentation, the setup and capability of beamline 12ID-B, a premier X-ray scattering
beamline of Advanced Photon Source at Argonne National Laboratory, will also be
discussed.
Figure 1. 3D structures of the iron nanoparticle derived from X-ray scattering data collected at various reaction time.

**COLL 418**

**Latest developments in X-ray nanochemistry**

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In this talk I will describe a few latest developments recently occurred in my lab in the field of X-ray Nanochemistry, which is to use nanomaterials to enhance the effect of X-rays. Examples of isolating type 1 and 2 physical enhancement and chemical enhancement, as well as the combination of these enhancements will be shown. The results demonstrate the benefit of isolation, optimization and combination of these individual enhancement mechanisms. Developments occurred recently in other labs will be briefly reviewed.

**COLL 419**

**Super-resolution imaging and spectroscopy of Au25 nanoclusters using two-photon excited fluorescence near-field scanning optical microscopy**

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Recent spectroscopic investigations on quantum-confined Au25 nanoclusters have begun to unravel their unique properties that were hitherto unclear to the scientific community. As an emergent class of nanomaterials, gold nanoclusters (<2.5 nm) possess significantly greater fluorescent quantum yields than that of gold nanoparticles (>3 nm) suggesting their potential use in super-resolution imaging and spectroscopy. Since the observation of unusually large two-photon absorption cross sections ($\delta=17,000$ GM per-atom) for Au25 nanoclusters in solution phase, it was not clear as to how $\delta$ of an Au25 nanocluster would change in the absence of a solvent or in a different dielectric medium (e.g. in air). Moreover, since the advent of near-field scanning optical microscopy (NSOM), fluorescent chromophores were imaged with effective breaking of Abbe’s diffraction barrier. However, until now aperture-based two-photon excited fluorescence (TPEF) NSOM was not reported to give point resolutions <175 nm. In our current work we report the TPEF NSOM imaging and spectroscopy of Au25 nanoclusters with 37 nm point-resolution. According to our understanding this is the first time that aperture-based TPEF NSOM has been able to elicit point resolutions <100 nm. Moreover, we were able to observe enhanced per-atom two-photon cross section values (~52,000 GM).
Additionally, we unveil a method that can be used effectively to obtain non-aggregated single nanocluster densities on a substrate which would stimulate further studies on single nanoclusters. Therefore, our current work introduces gold nanoclusters as a fluorescent nanomaterial that can be utilized in super-resolution imaging and an approach that can be used to conduct spectroscopy of single quantum-confined gold nanoclusters.

References

COLL 420

Surface enhanced Raman scattering based versatile quantitative detection using embedded internal reference

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Surface Enhanced Raman Spectroscopy (SERS) is an excellent tool that provides information about the vibrational modes of molecules. However, quantitative analysis using SERS has remained a challenge largely because of the difficulty in reproducing the SERS substrates. We report a facile synthesis method of SERS substrates with embedded internal reference that can be used as detection in condensed phase.
Quantitative SERS measurements using these internal standard embedded SERS substrates are successfully demonstrated with versatile analytes. The inclusion of an internal reference significantly improves the reliability and quality of quantification of the analytes. The scheme is versatile and has the potential for the detection of a wide range of analytes.

**COLL 421**

**Investigating lipid corona formation onto nanoparticle surfaces through fluorescence correlation spectroscopy**

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The unintended impact of nanomaterials when exposed to biological systems is a question of increasing importance, as various nanomaterial constructs are employed in the fields of medicine and biotechnology. During exposure, biological molecules, such as proteins, nutrients, and cellular components may adsorb to the nanomaterial, forming a corona. Thus, what is recognized by cells is the nanomaterial + corona complex, potentially resulting in a different response by the system than originally intended, leading to varying consequences. Therefore, understanding the interactions of nanoparticles exposed to a biological environment is crucial to determining the fate and potential impacts of nanoparticles to a living system. When nanoparticles come into contact with the cell or cell membrane components, it is possible that a lipid corona may form around the interfacial region. Lipid vesicles are a simple experimental model of cell membranes and can be systematically varied to probe the role of specific membrane properties such as fluidity and charge. Lipid vesicles of various size, composition, and charge are interacted with fluorescent nanoparticles of varying size and surface charge to understand the mechanism of lipid corona formation using fluorescence correlation spectroscopy (FCS). In addition to FCS experiments, time-resolved fluorescence quenching measurements aim to provide kinetic information on lipid corona formation. These studies are aimed at understanding and describing the adsorption behavior of lipids to nanoparticle surfaces.

**COLL 422**
Stable ferromagnetic nanoparticle dispersions: Surface modification of graphene coated nanomagnets allow stable dispersions of functionalizable ferromagnetic nanoparticles

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For many applications of magnetic nanoparticles such as for medical diagnostics, biotechnology, biomedical applications and magnetic biosensors, stable dispersions of magnetic nanoparticles in aqueous solutions are crucial. These dispersions are usually made from superparamagnetic iron oxide nanoparticles since they form stable dispersions and can simply be collected by application of an external magnetic field. A drawback is the low saturation magnetization of these particles which often leads to long separation times and incomplete particle recovery from dispersions. Ferromagnetic pure metallic nanoparticles show a substantially higher saturation magnetization but also show a considerable tendency to agglomerate. Thus, it is highly desirable to create a material which combines the advantageous properties of ferromagnetic (high saturation magnetization) and superparamagnetic (dispersion stability) particles.

Here, we describe the formation of a metal cobalt nanoparticle based ferromagnetic fluid with unprecedented dispersion stability and chemical functionality by specific covalent surface modification. More detailed, graphene protected metallic nanomagnets, prepared by flame spray synthesis, which are covalently functionalized on the particle surface via diazonium chemistry are shown. A block-copolymer is grown from the particle surface by SI-ATRP. This block-copolymer consists of a negatively charged polymer block that is responsible for the colloidal stability of the particles and a second polymer block, which allows post-modification of the particles. The length of both polymer blocks is crucial for the colloidal stability of the particles and is studied in this work. Post-modification of this material by introduction of azide-functionality followed by the well-known “click”-reaction, allows the attachment of various desired target molecules. These nanoparticles form stable dispersions in various aqueous solutions, including biological relevant buffer systems.

Substrate-induced broken degeneration of plasmonic nanoparticles: Dependence on wavelength and polarization

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Metal nanoparticles (NPs) experience collective oscillations of the electrons on their surface known as localized surface plasmon resonance (LSPR). The high LSPR tunability has allowed the development of a wide range of nanotechnology applications. For many practical applications and in order to understand many nanoscale phenomena the spectral analysis of single NPs is a demand. The gold standard technique for the spectral analysis of individual NPs is the darkfield microspectroscopy, where NPs are dispersed onto a substrate and subsequent spectroscopy is performed on each NP. Still, experimental studies about the effect of the substrate on the plasmonic properties of single NPs are scarce.

Here we study how the properties of single and dimer plasmonic gold NPs are affected when deposited onto high refractive index dielectric substrates, such as silicon surfaces, using a newly developed polarization-dependent dark-field spectroscopy technique. When a NP is bound to a surface, the degeneration of the plasmon modes parallel and perpendicular to the substrate is broken, which is confirmed by the polarized-resolved scattering spectra (Fig 1A) that shows multiple resonance peaks with a strong dependence on the incident light polarization. Moreover, the broken degeneration of parallel and perpendicular dipole plasmon modes is observed here for the first time as a change on the far-field scattering emission shape, as shown by the spatial scattering profile of single and dimer NPs shown in Fig 1B. Such experiments are only possible because the new technology has the capacity for the spectral characterization of
hundreds of single NPs with submicrometer spatial resolution in minutes.

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Figure 1. A) Scattering spectra of single and dimer NPs for different polarizations. B) Darkfield images (left) and scattering spatial profile (right) of single and dimer NPs at different wavelengths.

COLL 424

$^{31}$P CODEX NMR and phospholipid lateral diffusion in membranes
Lateral diffusion is a fundamental property of biological membrane components, important for a host of biomembrane functions. Recently, we demonstrated the use of \$^{31}\text{P} \text{ CODEX (Centre-Band-Only-Detection-of-Exchange) NMR}$ to measure lateral diffusion of phospholipids in spherical lipid bilayer vesicles. This method requires no labeling of the species of interest, can be applied in different thermotropic and ordered/disordered lipid phases, and permits multiplexing, i.e., simultaneous measurements on multiple phospholipid species. Our most recent efforts have focused on: 1) experiments performed with a “gold standard” phospholipid, dimyristoyl phosphatidylcholine (DMPC), that allow ready optimization of sample properties and measurement conditions so as to yield maximally efficient lateral diffusion measurements, and 2) development of a rigorous powder average simulation protocol to extract the lateral diffusion coefficient from such CODEX data with high fidelity.

**COLL 425**

**Exploring the interactions of ions with fluid lipid bilayers**

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Metal cations can bind to the surface of biomembranes and change the physical properties of the lipid bilayer and the associated interfacial water structure. Both
spectroscopic and microscopy data will be presented to show how ions bind and how this, in turn, influences the structure of interfacial water molecules. Studies will be presented both as a function of the nature of the cation and with different head group chemistries within the lipid membrane. Also, results will be shown with different tails groups. Interestingly, the alkyl chain length and temperature at which experiments are performed can have a substantial influence on the binding process.

**COLL 426**

**Droplet interface bilayer: A model for biomembrane water permeability studies**

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We report results that illuminate the exquisite interplay among factors mediating the rate of water transport across the bilayer interface. Using the droplet interface bilayer as a model biomembrane, we correlate the structure of various amphiphilic molecules at an aqueous microdroplet interface with their function to facilitate osmotically-driven water transport across the interface. Key parameters pertaining to permeability provide important insights into the aggregate structure of these soft membranes.

**COLL 427**

**Molecular dynamics study of pore formation by melittin in 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) and 1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phospho-(1'-rac-glycerol) (DOPG) mixed lipid bilayer**

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Melittin is a naturally occurring antimicrobial peptide that has the ability to kill bacterial cells through cell membrane penetration leading to pore formation. In this investigation, all atom molecular dynamics (MD) simulation has been carried out to describe the interaction of different number of peptides placed on the surface of 3:1 ratio of 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC) and 1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phospho-(1'-rac-glycerol) (DOPG) lipid bilayer (a mimic of bacterial cell membrane). MD simulation was also carried out for different number of transmembrane peptides in a 3:1 ratio of DOPC/DOPG mixed membrane as well as for pure DOPC lipid bilayer (a mimic of mammalian cell membrane). Broadening of phospholipid head regions in the bottom leaflet as well as thinning of membrane were found to occur for melittin placed on the top leaflet only for mixed membrane. Critical P/L ratio was observed for penetration of melittin from the surface as well as for water channel formation for transmembrane peptides. The phospholipid density profile across the bilayer indicated a toroidal pore structure. The behavior for mixed and pure membranes was found to be similar for transmembrane peptides thus implying high toxicity of melittin. A
mathematical model for the evaluation of energy barrier for formation of pore consisting of peptide aggregates of different size interspersed with phospholipid head was proposed which considers detailed pore structure as well as intermolecular interactions. Umbrella sampling was employed to calculate the free energy of formation of pores consisting of different number of transmembrane peptides using MD simulation. These were compared with model predictions.

COLL 428

Gold nanoparticle – lipid nanodisk self-assembly: Insights from computer modeling

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There is a growing interest in applications of gold nanoparticles in nanobiomedicine. To ensure long-time circulation and controlled delivery, gold nanoparticles typically require functionalization and/or encapsulation into nanocarriers. The understanding of interactions between gold nanoparticles and lipids is obviously important for designing lipid nano-carriers and applications of gold nanoparticles involving their internalization by cells. Computer modeling is capable of providing valuable insights in this area. Using coarse-grained molecular dynamics simulations with a Martini force-field we investigate the interactions between hydrophobically-modified gold nanoparticles and a mixed lipid bilayer, a nanodisk composed of short and long lipids or a vesicle. While experimentally one can estimate the overall degree of encapsulation and stability of aggregates containing gold nanoparticles, the molecular details of interactions between nanocarrier and gold nanoparticles remains obscure. We investigate the equilibrium structure of self-assembled lipid with encapsulated single or multiple gold nanoparticles and analyze the effect of lipid composition (i.e. fraction of short to long lipids) on the outcomes of gold nanoparticle encapsulation. Furthermore we will also discuss the interaction between encapsulated gold nanoparticles as a function of gold nanoparticle size and length of hydrophobic tethers attached to gold nanoparticles. The stability and equilibrium structure of lipid carriers with encapsulated gold nanoparticles will be tested at different temperatures and in the presence of cholesterol, which is one of the natural components of a cell surface. The results of computer modeling will be compared with available experimental data and conclusions will be made regarding the influence of the intrinsic properties of lipids and gold nanoparticles on the equilibrium structure and stability of lipid/gold nanoparticle aggregates.

COLL 429

Novel scattering methods reveal structure of single supported lipid membranes

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Over the past several decades, supported lipid membranes have been used as model systems of cellular membranes, to investigate various membrane interactions, and as platforms for development of bio-sensors. Precise structural characterization by x-ray reflectivity and grazing incidence diffraction at the solid-liquid interface offers a wealth of insight into membrane organization, self-assembly, and domain formation as well as how membranes respond to changes in their environment. In this talk, I will discuss some recent advances in our understanding of supported membranes including (1) high resolution details regarding the inorganic-organic interface; (2) changes in the membrane structure with fabrication method, temperature, and solution conditions; and (3) a novel, “textured” lipid phase induced by specific-multivalent protein binding to membrane embedded receptors. The talk will particularly highlight the importance of x-ray scattering techniques for single, lipid bilayer structural characterization.

**COLL 430**

**Cyclic cyclosiloxane bound silver nanoraspberries**

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Morphologically controlled noble metal nanoparticles are of wide interest due to their quantum mechanical, optical, conductive, catalytic, and SERS properties. Is it well established that metallic nanoparticles are unstable due to their differences in band gap
energies that result when transitioning from bulk to nanoscale. Such particles can be stabilized in presence of appropriate surface ligands. In our laboratory, we explore a family of silicone based systems for the generation of metallic nanoparticles, specifically cyclic siloxanes with repeating Si-O-Si linkages. In our previous work, we have demonstrated that cyclic and linear siloxanes provide unaltering stabilization while still preserving the reactivity of the nanoparticle [1, 2]. Despite their potential for different silicon chemistries, cyclic siloxanes have not been thoroughly investigated for the generation of nanoparticles.

In this talk, we will demonstrate the first one-pot synthetic approach which utilizes a dual action oligo-cyclicsiloxanes as a reducing and stabilizing agent for the production of novel metal nanoparticles. The reactivity of SiH bonds of cyclic siloxanes have not been successfully exploited as a potential site for siloxane functionalized nanoparticles. In this presentation, emphasis will be placed on nanoparticle morphologies which ultimately become unstable over time due to steric hindrance of the cyclic molecule. In order to sustain the stability, solubility, and structure of the nanoraspberries, additional long chain hydrosilanes are investigated as supplementary stabilizing agent and as well as a ligand exchange molecule [2, 3]. In addition, we will disclose this further functionalization of the raspberries renders these nano objects as silicon-based building blocks for a new class of hybrid nanomaterials.


COLL 431

Modulation of biomineral crystal growth and assembly by polymeric matrices

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Biominerals found in living organisms have diverse biological functions and unique properties arising from the particular structure, orientation, and morphology of the constituent minerals. A systematic investigation of the morphological evolution of biominerals grown in organic matrices, and the interaction of such matrices with the inorganic crystals are essential for understanding biomineralization processes and for developing bioinspired materials. We employ here hydrogels as model organic matrices and a ‘double-diffusion’ method to mimic the formation of calcium oxalate, the major constituent of kidney stones. Gel-mediated crystallization provides a great way to vary the local supersaturation through controlling the diffusion rate of the reacting ions. We
study the nucleation, growth, type of polymorph, orientation and aggregation of the calcium oxalate particles as affected by the gel density, reservoir concentrations, molar stock solution ratio, and additives. The obtained crystals are characterized for their morphology, crystal structure and composition using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), FTIR and Thermogravimetric Analysis (TGA). These findings help our understanding of the mechanism of polymer incorporation in biomineral aggregates, and provide insights into the formation of organic-inorganic composite materials.

COLL 432

Hyaluronic acid-based hydrogels with network-disruptive dangling ligands for the assembly of acinar spheroids

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Culturing human salivary acinar-like cells (hSACs) in hyaluronic acid (HA)-based hydrogels is a promising approach to engineer functional salivary glands. Traditionally, the mechanical properties of HA hydrogels are tuned by varying the concentration and percent functionality of chemically derived HA precursors. Our research focused on tuning hydrogel matrix architecture to increase solute diffusion and enhance cell mobility while maintaining overall network integrity. We utilized the high crosslink density imparted by low molecular weight HA, while relying on tethered peptides, identified from extracellular matrix (ECM)-derived perlecan domain IV, fibronectin and laminin, to alter topology and morphology of the networks while additionally presenting biological cues. Specifically, an acrylate moiety was incorporated to low molecular weight (5 kDa) HA and the thiol functionality was introduced to high molecular weight (500 kDa) HA. The resulting HA network, established via a Michael-type addition reaction, possesses covalently tethered dangling ligands that disrupt the regular molecular network. hSACs encapsulated in these hydrogels remain viable and aggregate to form acinar spheroids reminiscent of the native tissue. To distinguish the contribution from the tethered ligands, be it from cellular cues or network defects, bioactive active and inactive ligands of the same composition, were incorporated. Overall, this strategy produced an ECM-modified irregular network structure suitable to promote hSAC viability, cell migration, spheroid assembly, and early aspects of tissue morphogenesis, thus a step forward in tissue engineering of salivary glands.

COLL 433
Transglutaminase catalyzed PEGylation of alginate microgels for islet cell encapsulation

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Transplantation of polymer-encapsulated cells has shown promise in alleviating the symptoms of diseases such as type-1 diabetes. In order to increase stability of pancreatic islets encapsulated in alginic acid microgels polycations are adsorbed onto the outer surface; however, the adsorbed polycation coating is susceptible to desorption, leading to breakdown of the divalent cation cross-linked alginic acid core. Herein we present an enzymatic technique to covalently bond poly(ethylene glycol) (PEGylation) to crosslinked alginic acid microgels. Traditional covalent cross-linking techniques involve radical polymerization with harsh chemicals or reagents; our enzymatic technique instead takes place in physiological buffers at 37 °C. Alginic acid was functionalized with L-glutamine methyl ester, followed by purification and confirmation of conjugation with NMR. A mixture of functionalized alginic acid and beta cells were extruded into a gelling bath containing divalent ions to form cross-linked alginate microgels. Transglutaminase in the presence of calcium was used to catalyze covalent conjugation of poly(ethylene glycol)bis-amine ($n$, 10,000 g/mol) onto L-glutamine methyl ester’s amide groups on the alginate microgel surface (1-2 mm). We confirmed encapsulated cell survival post-PEGylation using a live/dead fluorescent assay kit. To characterize the extent of PEGylated surface coverage on the microgels its methoxy backbone was immunofluorescently labeled and imaged using an inverted confocal microscope. Encapsulated beta-cell functional was quantified using a glucose challenge and insulin ELISA. We anticipate this device will have greater long-term stability than devices lacking polymer coatings or having adsorbed polycation coatings. Its intended use is as a bioartificial pancreas to replace daily insulin injections.

COLL 434

Copolymer nanoparticles via RAFT emulsion polymerization: Synthesis, characterization, and interfacial activity

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A poly(glycerol monomethacrylate) (PGMA) macromolecular chain transfer agent has been utilized to polymerize benzyl methacrylate (BzMA) via reversible addition-fragmentation chain transfer (RAFT)-mediated aqueous emulsion polymerization. This formulation leads to the efficient formation of spherical diblock copolymer nanoparticles.
at up to 50 % solids. The degree of polymerization (DP) of the core-forming PBzMA block has been systematically varied to control the mean particle diameter from 20 nm to 193 nm. Conversions of more than 99 % were achieved for PGMA_{51}-PBzMA_{250} within 6 h at 70°C using macro-CTA/initiator molar ratios ranging from 3.0 to 10.0. DMF GPC analyses confirmed that relatively low polydispersities (M_w/M_n < 1.30) and high blocking efficiencies could be achieved. These spherical nanoparticles are stable to both freeze-thaw cycles and the presence of added salt (up to 0.25 M MgSO_4). Three sets of PGMA_{51}-PBzMA_x spherical nanoparticles have been used to prepare stable Pickering emulsions at various copolymer concentrations in four model oils: sunflower oil, n-dodecane, n-hexane and isopropyl myristate. A reduction in mean droplet diameter was observed via laser diffraction on increasing the nanoparticle concentration. Finally, the cis diol functionality on the PGMA stabilizer chains has been exploited to demonstrate the selective adsorption of PGMA_{51}-PBzMA_{100} nanoparticles onto a micro-patterned phenylboronic acid-functionalized planar surface. Formation of a cyclic boronate ester at pH 10 causes strong selective binding of the nanoparticles via the cis-diol groups in the PGMA stabilizer chains, as judged by AFM studies. Control experiments confirmed that minimal selective nanoparticle binding occurred at pH 4, or if the PGMA_{51} stabilizer block was replaced with a PEG_{113} stabilizer block.

**COLL 435**

**Light sensitive smart nanocontainer**

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Stimuli responsive smart containers have been studied for frontier technological applications, such as drug delivery, energy storage, and molecular imaging. These synthetic containers have an inner cavity that is able to hold small molecules, and their
gated semi-permeable surfaces allow for the controlled exchange of these small molecules between solution and the inner space. Virus-like particles (VLPs) have a distinct advantage as smart nanocontainers because of their monodispersity, biocompatibility, and biodegradability, etc. This research project has focused on using bacteriophage Qβ as an environmentally sensitive nanocontainer. Qβ is an icosahedral capsid that is self-assembled from 180 identical coat proteins, which form 20 large pores (~3nm) and 12 small pores (~1.9nm) on the surface. These pores are large enough to allow small molecules to diffuse in the cavity from the surroundings. In this project, disulfide bonds along the pores have been used as the functional handles to attach synthetic molecules. We have been developing different bioconjugation methods that can functionalize disulfide bonds without disturbing the virus’s quaternary structure. Current results have shown that rebridged virus particles maintain their original shape and their native thermal stability. In addition, azobenzene compounds have been attached along the pores using our new bioconjugation methodology. By utilizing the photoisomerization of azobenzene, the pores will be switchable under UV light at the appropriate wavelength.

COLL 436

Encapsulation of upconversion materials by heterophase methods

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TTA–UC is the only upconversion process excited with non-coherent sunlight. Extremely low excitation intensity, necessary for efficient TTA–UC emission, combined with substantially red-shifted excitation wavelength (fitting into the tissue-transparency window) explain the significant research efforts, attracted from this UC process in the last few years.[1,2] The TTA–UC process is based on energy exchange between excited sensitizer/emitter triplet states. Therefore, any present oxygen contamination will cause depopulation (via oxygen quenching) of those triplet states and will decrease the TTA–UC efficiency drastically. The main aim of our work is to encapsulate upconversion couple (PdOEP/Perylene) for the direct application of the triplet-triplet annihilation photon energy upconversion (TTA-UC) process in confinement targeting biomedical applications. The important challenge in this work is to protect the TTA-UC process from the molecular oxygen and to obtain efficient generation of high energy photons.

The UC-couple was encapsulated in poly(styrene/acrylic acid) and poly(styrene/2-aminoethyl methacrylate hydrochloride) nanocapsules. Two principal approaches to protect the nanocapsules from oxygen are presented. The first approach is the synthesis under oxygen-protective conditions (i.e., complete darkness and argon atmosphere) to exclude the oxidation of the emitter molecules caused by singlet oxygen, generated during the synthesis at daylight conditions and oxygen-rich environment.[3] The second approach is the armoring of the nanocapsules in two simultaneously occurring processes: a) a deposition of preformed silicate platelets on
the surface of the oppositely charged nanocapsules, and b) a sol-gel process that "closes" the structure and eventually avoids the entry of oxygen from the external environment.

References

COLL 437

Chymotrypsin immobilized onto surface functionalized macro and nanoscale Nylon 6,6 solid supports

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Enzyme immobilization has been shown to widen the working parameters (e.g. temperature, pH) of enzymes. Direct enzyme modification serves to improve incorporation with materials for immobilization, but often results in large activity loss. Although carrier-bound enzymes often have expanded optimal working conditions, the activity retention for these systems is low in comparison to free native enzyme due to limited protein loading, limited access to substrate, and non-ideal orientation to the solid support. Many water-insoluble polymer carriers are hydrophobic and influence unfavorable enzyme positioning when immobilized. This work describes the immobilization of chymotrypsin to Nylon 6,6, a water-insoluble synthetic polymer, as electrospun nanofibers and planar films to showcase the benefits of nano-scale materials when compared to traditional immobilization onto macro-scale solid supports (i.e. planar films and agarose gels) in order to overcome their common limitations. Electrospinning effectively creates nano-scale materials where the final morphology is dependent on variation of parameters including polymer concentration, polymer flow rate, and voltage. This method is highly scalable for industry use, and can be applied to many polymer and biopolymers. The surface modification method for both the planar films and nanofibers employed amine groups present from the Nylon 6,6 to form amide bonds with aldehyde based cross-linkers. Electrospun Nylon 6,6 nanofibers had an average fiber diameter of 284 ± 18 nm with 1.625 μg of conjugated protein per mg of nanofiber. Chymotrypsin on nanofibers retained up to 58.36% activity of native enzyme. The activity retention of chymotrypsin immobilized by the same chemical method onto planar films was 0.74%. Immobilization to nano-scale polymer materials effectively increases the surface area to volume ratio of a solid support, and may allow enzymes to experience reduced lateral interaction with neighboring proteins, in effect creating a
microenvironment that is similar to that of free native enzyme. Here, chymotrypsin benefits from immobilization onto nano-scale solid supports, while having the potential for simple processing incorporation, recovery, and reuse on water-insoluble Nylon 6,6.

COLL 438

Seeding metal-organic frameworks on Nyco fabric using atomic layer deposition: Opportunities for soldier uniforms with integrated chemical hazard mitigation

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Metal-organic frameworks (MOFs) are highly ordered porous materials that offer higher gas adsorption, storage, and reactivity towards hazardous gas streams than traditional porous materials such as activated carbon. MOF materials have the potential to provide revolutionary advances in filtration, gas storage and hazardous chemical capture and decomposition. However, conventional solvothermal synthesis methods are not easily adapted for MOF integration. In order to expand the useful application of MOFs, new techniques are needed to grow MOF materials directly onto existing filtration media and textile-based platforms.

Recently we showed metal oxide thin films grown by atomic layer deposition (ALD) can promote growth of a MOF referred to as HKUST-1 (Cu₃BTC₂) on various non-woven fiber substrates including polypropylene, cotton, and polybutylene terephthalate. Of interest to the Army is adding new functionality to currently approved textile platforms such as Nyco fabric. Nyco is a woven 50/50 blend of nylon and cotton fibers and is widely used in military uniforms and other garments. We found the HKUST-1 mass loading and overall BET surface area was improved when thin nanoscale coatings (<10nm) of Al₂O₃, ZnO and TiO₂ were deposited onto the Nyco prior to MOF growth. One major challenge for growing MOFs on Nyco is the degradation of nylon in hot acid solutions. We found our ALD metal oxide coatings can protect the nylon fibers during subsequent MOF growth and provide a starting layer to promote MOF nucleation. In this presentation we will compare the nucleation, growth and adhesion of HKUST-1 on Nyco fabric coated with ALD Al₂O₃, ZnO and TiO₂ and discuss applications of MOFs on fibers for capture of ammonia and other toxic substances.

COLL 439

Water-soluble polyelectrolyte complexes as safe flame retardant nanocoating for woven fabric
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. Waters-soluble polyelectrolyte complexes (WPEC), 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. When combined with melamine, nylon-cotton (NYCO) blended fabric is able to pass a standard vertical flame test, involving a 12 s exposure to direct flame (ASTM D6413). These are the types of fabrics widely used in the military, industrial workwear, etc. This water-based coating technology can be applied quickly and easily in just one or two steps.

COLL 440

Computationally aided design of self-decontaminating multicatalyst polyelectrolyte membranes (MC-PEM)

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We are developing a multi-catalyst polyelectrolyte membrane (MC-PEM) with the purpose of blocking and detoxifying chemical warfare agents (CWA). When incorporated into a wearable garment, these membranes will be capable of prolonging the time one can be exposed, without causing harm, by being permeable to water while simultaneously acting as a barrier against CWA. Polyelectrolyte membranes (PEM) are employed as the host material for integration of catalytic nanoparticles capable of decomposing CWA susceptible to oxidation and/or hydrolysis. A thorough understanding of the catalytic activity and diffusion properties of these membranes are investigated through experimental means by x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and x-ray photoelectron spectroscopy (XPS). The efficiency of the membrane is tested against simulants such as DMMP using nuclear magnetic resonance (NMR) and droplet sorption experiments. In tandem, a multi-scale modeling approach has been applied to gain fundamental insight towards MC-PEM design and optimization. This includes ab initio measures, i.e. density functional theory (DFT), to study the mechanism of surface adsorption and decomposition on different crystallographic planes in order to determine the overall
catalytic effectiveness of the nanoparticles. Molecular dynamics (MD) simulations are utilized to explore the mechanisms of sorption and diffusion of species, such as sarin, through the PEM at different hydration levels, as well as how external factors such as strain and temperature may affect the PEM host matrix that houses the catalytic nanoparticles. Finally, canonical ensemble dissipative particle dynamics (DPD) simulations and Monte Carlo (MC) simulations have been performed to gain insight to the transport and sorption properties of the hydrated membranes.

COLL 441

Autonomous, adaptive, responsive, and modular second skin based on organohydrogels

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The performance of tasks while wearing chemical biological (CB) protective clothing is a challenge. Efforts are underway to develop materials for CB protection that are lighter in weight and impose reduced thermal burden. The ideal protection would be provided by what amounts to a "Second Skin." In its normal state the Second Skin would allow air and moisture transport through it. Upon exposure to a hazardous chemical or biological
the Second Skin would sense the presence of the hazard, transduce a response to adapt into an active protection state, neutralize the hazard, and return to its normal, benign state following the incident. The main objective of this work is to develop adaptive, responsive materials toward such a Second Skin, with the material design based on the use of organohydrogels (OHGs), other hydrogels (HGs), and catalysts. These modular, responsive gels will provide the sensing, transduction, protection, and decontamination functions to the material in an autonomous manner. The gels will be integrated into a lightweight substrate, such as a nonwoven fabric. The surface layer of the material will contain threat-detecting nanoparticles functionalized with CB sensing elements, enabling the specific detection of agents and generation of a reporter signal to trigger activation which will lead to a protective state. OHGs, produced from nanoemulsions, have been developed which have demonstrated the ability to sense the presence of hazardous chemicals and to destroy or sequester the hazard. Other HGs have demonstrated complimentary effectiveness. Surface multifunctionality involving various catalysts has demonstrated additional sensing and hazard neutralization. Swelling of the gel particles within the nonwoven fabric will block the existing pores, leading to increased barrier properties and increased protection. With this multifunctionality the Second Skin is expected to provide responsive protection against a variety of hazards including blister agents, nerve agents, spores, and toxins.

COLL 442

Water-based flame retardant multilayer nanocoating for polyester-cotton

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This presentation will highlight a new flame retardant nanocoating for polyester-cotton fabric. Layer-by-layer assembly is used as a water-based and environmentally benign method to deposit a highly effective flame retardant onto this widely used clothing fabric. Using chitosan and an insoluble phosphorus source in alternating layers, less than 15 wt% coating is necessary to impart self-extinguishing properties to the fabric. Immediate self-extinguishment in the vertical flame test and a significant reduction of peak heat release of the fabric are the result of this coating. This commercially-feasible and environmentally-benign technology imparts a flame retardant treatment to one of the most commonly used fabric types.

COLL 443

Photocatalytic and gas sensor properties of metal oxide-decorated polypropylene swatches

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Polypropylene swatches (i.e., knitted or non-woven fabrics) have been prepared by melt extrusion from fibers of various geometries, including bi-component (sheath/core) ones. Metal oxides have been placed on the surfaces of these fibers either by adding them to the melt or by post-functionalizing pure polymer swatches. One method of post-functionalization includes plasma treatment and subsequent immersion in colloidal metal oxide suspensions. Using these methodologies, titanium dioxide, zinc oxide, and zirconium oxide and their mixtures have been deposited on the fiber surfaces. The resulting swatches have been characterized using electron microscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy, diffuse reflectance spectroscopy, and fluorescence measurements. The swatches display interesting optical properties, including fluorescence from the metal oxides. In the case of zinc oxide, the ratio of the UV and visible fluorescence peaks changes upon exposure to certain gases, including methanethiol. The photocatalytic oxidative efficiencies of the functionalized swatches have been investigated using rhodamine b and malathion, and they show high efficiency toward the decomposition of these molecules. Possible applications of this research related to hazardous chemical detection and decontamination are discussed.

COLL 444

Delivery of chemically modified proteins to the nucleus of cells

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Direct delivery of proteins to the nucleus holds great therapeutic potential. However, lack of cytosolic access of the delivered protein remains a major hurdle. Herein, we describe a strategy for rapid and effective delivery of proteins using a nanoparticle stabilized capsule (NPSC) delivery system. This system is formed and stabilized through supramolecular interactions between the nanoparticle–protein cargo shell and the fatty acid core. We have demonstrated the utility of this platform for intracellular targeting: proteins chemically modified with nuclear targeting labels are rapidly delivered into cytosol of cells by NPSCs and significantly accumulate in the nuclei of cells. We will discuss the import of these chemically modified proteins to nucleus and underlying mechanisms.
How nanoparticle design affects targeting selectivity: Insights from computer modeling

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One of the areas of active development of modern nanomedicine is application of polymer tethered nano-size carriers for drug/gene delivery and imaging purposes. Usually nanoparticles are functionalized by ligands, aptamers or antibodies capable of specific interactions with cell surface receptors. Still many cells can possess the same receptors, even if with different expression level, which makes it challenging to achieve selective targeting of particular cells. Thus, strong interactions of targeting moieties of nanoparticles with receptors while ensuring stable attachment of nanoparticles to cell surfaces often compromises targeting selectivity as nanoparticles get attached to any surface possessing a targeting receptor. So far the search for improved nanoparticle selectivity has been directed toward better matching of targeting groups to specific receptors. Considerably less attention has been paid to the design of the nanoparticle itself and its influence on targeting selectivity. Obviously, nanoparticle design is much easier to control and understanding how the design can influence the selectivity of targeting becomes increasingly important as development of nanoparticulate formulations progresses from the laboratory stage to clinical testing. Computer simulations allow a systematic investigation of the influence of multiple factors and provide a unified platform for the comparison of the efficiency of different nanoparticles for a given cell surface or analysis of selectivity of a nanoparticle towards cells with
different receptor densities. We investigate the influence of the nanoparticle physical and biochemical properties (such as nanoparticle size, polymer tether length and density, ligand density and valence) on the selectivity of nanoparticle-cell surface interactions and make experimentally testable predictions regarding the ways to enhance selectivity of nanoparticle-cell surface interactions by optimizing the nanoparticle architecture, which will be discussed during the talk.

**COLL 446**

**DNA-conjugated silicon nanoparticles for the detection of MicroRNA-21**

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There is much current interest in the development of DNA hybrid nanomaterials. These systems not only inherit the unique biomolecule recognition property of Oligonucleotides (ODNs) but exhibit more advantages over free ODNs, such as, enhanced nuclease resistance, increased binding affinity to target sequences, and high cellular uptake potential. Among various DNA hybrid nanosystems, the construction of water soluble, heavy-metal free, silicon nanoparticles (SiNPs) conjugated with DNA is an attractive endeavor because some traditional systems (e.g., Au, Ag, CdSe, Fe₃O₄) involve the use of heavy metal inorganic nanoparticles that can limit their potential biological usage. On the other hand, silicon nanoparticles are found to be biocompatible, biodegradable, and earth-abundant. Herein, we introduce a facile two-step synthesis—from bulk silicon wafer—to prepare SiNP ODN conjugates featuring reactive high-energy ball milling (RHEBM) and thiol-ene click chemistry. In addition, we also demonstrate the functionality of such SiNP ODN conjugates by detecting an important cancer biomarker, microRNA-21.

**COLL 447**

**Role of nanogold apoE reconstituted vehicles (NERVs) as potential drug delivery systems**

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Poor aqueous solubility and targeted delivery continue to offer challenges in drug delivery. In this study, we have developed a novel multifunctional platform that not only addresses both issues, but offers therapeutic advantage as well. We integrate apolipoprotein E3 (apoE3), a human plasma apolipoprotein that serves as a high-affinity ligand for the low density lipoprotein receptor (LDLr) with gold nanoparticles (AuNP), which are highly hydrophobic, water-insoluble nanomaterials, to form two types of Nanogold-apoE3 Reconstituted Vehicles (NERVs): (i) apoE3 coated gold nanoparticles (ECGNP) using lipid-free apoE3, and, (ii) reconstituted high density lipoprotein-AuNP (rHDL-AuNP) nanodiscs bearing gold nanoparticles. The ECGNP were generated by
flash nanoprecipitation and the rHDL-AuNP by liposome preparation followed by incubation with recombinant apoE3 bearing a hexa-His tag. Unbound AuNP and protein-free lipid vesicles were separated from NERVs by magnetic beads technology. UV-Vis spectra indicated the presence of stable particles with surface plasmon band at ~520 nm, a signature feature of AuNP. Transmission electron microscopy revealed that the particles were spherical and monodisperse, with ECGNP bearing a particle diameter of 3.36 ± 1.19 nm; the rHDL-AuNP were found to be 22-45 nm diameter with a AuNP core of 3.12 ± 0.91 nm. Co-immunoprecipitation assay using a soluble form of the LDLr indicated binding of NERVs to the LDLr. Finally, immunofluorescence analysis of glioblastoma cells by confocal microscopy revealed the presence of fluorescent, peri-nuclear endocytic vesicles in both cases, suggesting cellular uptake of NERVs by receptor-mediated endocytosis. The findings that apoE3 (i) acts as a detergent in solubilizing and dramatically improving the aqueous solubility of AuNP, and, (ii) facilitates cellular uptake via receptor-mediated endocytosis by the LDLr pathway, are significant since they offer an effective means of delivering AuNP across the cell membrane. This is particularly relevant in tumor cells since they overexpress LDLr to meet the demands of high cholesterol that is required for rapid proliferation and membrane biogenesis. We take advantage of the high expression levels of the LDLr by the glioblastoma cells for targeted delivery of AuNP.

**COLL 448**

*Magnetization relaxation of magnetic nanoparticles for hyperthermia in live cells: Non-invasive monitoring*

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When magnetic nanoparticles (MNPs) are exposed to an alternating magnetic field, they can generate heat. This approach has been successfully employed in a selective destruction of cancer cells – known as magnetic hyperthermia. The amount of heat generated is strongly influenced by magnetization relaxation mechanisms, which can be altered by cellular microenvironment. In this study a novel application of AC susceptometry was used to follow the *in situ* magnetic response of model systems of blocked and superparamagnetic nanoparticles. The magnetisation relaxation was investigated in cell culture media, following cellular internalization in live osteosarcoma cells, and after subsequent freeze-thaw lysis. The AC susceptibility signal from internalised particles in live cells showed only Néel relaxation, consistent with measurements of immobilised nanoparticle suspensions. This emphasises the importance of such intrinsic magnetic properties for hyperthermia applications when particle mobility cannot be guaranteed. However, Brownian relaxation was restored after cell lysis, indicating that the immobilisation effect was reversible and that nanoparticle integrity was maintained in the cells. The results presented demonstrate that cellular internalisation can disable Brownian relaxation, which has significant implications for designing suitable nanoparticles for magnetic hyperthermia applications.
Further to this, the results also indicate that magnetic nanoparticles could be released from degrading cells following hyperthermia treatment in reusable form, and subsequently re-internalized by live cells.

**COLL 449**

**Boron- and gadolinium-rich nanoparticles for cancer treatment using neutron capture therapy**

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Neutron capture therapy (NCT) is a suggested treatment for cancer. Species with large amounts of boron-10 or gadolinium-157 are required for an effective NCT. Gadolinium-containing nanoparticles might also be useful in MRI imaging, thus allowing to create theranostic nanoconstructs.

We will describe three methods to prepare biocompatible boron-rich nanoparticles, by modifying the surface of boron nanoparticles (BNPs) with dopamine molecules, by encapsulating BNPs in a silica shell, and by grafting polymer brushes carrying carborane moieties on the surface of silica nanoparticles. Dopamine-modified BNPs are prepared by ligand exchange on the surface of hydrophobic BNPs formed by ball milling.

The boron core-silica shell nanoparticles are prepared by first performing a hydrosilylation reaction to convert the double bonds of the hydrophobic BNP ligands into trialkoxysilane moieties, followed by a sol-gel reaction to form the silica shell. The latter imparts hydrophilicity to the boron nanoparticle and provides a surface that can be further modified with various functionalities for targeted delivery. Furthermore, silica encapsulation results in particles that are uniform in shape and size, and are easy to manipulate.

Silica nanoparticles (SNPs) grafted with carborane-containing polymer brushes are prepared by modifying the silica surface with initiator moieties, followed by surface-initiated atom transfer radical polymerization of reactive monomers. After the formation of the polymer brushes, they are treated with carboranyl alcohols or acids, resulting in an almost complete modification of the polymer side-chains with the carboranyl moieties.

Finally, we prepared organically modified silica (ORMOSIL) colloidal particles with internal functional groups and microporosity, suitable for the incorporation of modalities for both MRI imaging and cancer treatment by neutron capture therapy using boron-10 and gadolinium-157 nuclei. These modalities were incorporated by preparing ORMOSIL particles with reactive functional groups throughout the nanoparticle body, followed by their conversion into the metal chelating and boron-containing moieties inside the nanoparticles.

**COLL 450**

**Smart surfaces for distinguishing epithelial cells and lymphocytes in laminar flow**
The present work demonstrates the use of nanoscopic walls to sort, capture or distinguish cells in laminar flow. Those cell line models are non-tumorigenic breast epithelials (MCF10A) and lymphocytes (Jurkat). Surfaces are developed to adhesively discriminate the dominant cells in milk (lymphocytes, epithelials), employing cell lines as a first model to guide subsequent development of surfaces targeting primary cells. The supernatant of centrifuged milk contains fats and protein molecules which could compete with cells for collecting surfaces. This study focuses on developing surfaces that avoid adsorption of these suspended milk molecules over the range of surface parameters where cell adhesion is important. Differences between epithelials and lymphocytes, especially their size, but also their softness and localized distribution of charge and other surface functionality are expected to be sufficient to enable discrimination. Rather than relying on expensive, fragile biomolecular fragments, the proposed surface would accomplish adhesive selectivity for targeted cells through the incorporation of robust, inexpensive and weakly-adhesive elements. This works also focuses on the motion of cells as they are capture (or not) by surfaces of different adhesive character. Scrutiny of the motion signatures of individual cells interacting with the patchy surfaces revealed that for some composition of surface heterogeneity and processing conditions (shear rate and ionic strength), cells rolled over the surface, while in other instances they arrest or did not interact at all with the surface. We also present economical, non-biomolecular surfaces with cell-specific adhesive character, assessing the intrinsic surface selectivity for near-surface flowing cells.

COLL 451

Synthesis of biocompatible thermoresponsive PEGMA nanoparticles for dual release

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Smart drug delivery platforms has been a critical research topic in recent years. Nowadays, chemotherapy is the most commonly used for the treatment of cancer. Although it is an effective treatment for many types of cancer, chemotherapy often results undesirable side effects and produce toxicity even at the usual doses. Anti-cancer drugs destroy both cancer and normal cells. Killing normal cells can cause unpleasant side effects, therefore there is an urgent need for novel techniques. In recent years, controlled drug delivery systems which are responsive to an external
trigger (i.e., pH, heat or light) make it possible to solve the problems encountered in the chemotherapy. Yavuz et al. demonstrated a platform based on Au nanocages covered with smart thermosensitive PNIPAM-co-AAm polymers for controlled release with near-infrared light. The dosage of the released cargo was controlled by manipulating the power density or irradiation time of light.

In this study, for the first time, we showed thermoresponsive and biocompatible PEGMA nanoparticles (NPs) with biodegradable disulfide crosslinker as drug delivery carriers. Two different dye molecules (rhodamine and PEG-Alizarin) were loaded to PEGMA NPs that give UV absorbance peaks at different wavelengths. We successfully investigated dual dye release property of PEGMA nanocarriers by temperature effect and dithiothreitol (DTT) degradation. This new system allows a dual release of different cancer drugs or biological materials at different times.

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REFERENCES

COLL 452

Zwitterionic bionanointerface: From cell membrane to protein mimic

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A great promise for nanotechnology in medical applications has focused on the development of different forms of nanoparticles for cancer therapy. However, for further biomedical applications, these nanoparticles should not only be high colloidal stable and biocompatible in the physiological environment, but also present targeting to tumor cells.

We explore to solve this problem by take advantage of the phosphorylcholine (PC), which is the natural molecules present the out most of cell membranes. For the first time, to our knowledge, we demonstrate that the covalent conjugation of PC onto GNs not only brings better dispersion stability than the neutral EG4, but also leads to targeting cell uptake within cancer cells. Considering that most cancer cells have over
expressed choline acceptors and present more aspiration of choline than normal cells, phosphorylcholine was explored here as a versatile ligand for selective uptake of GNs by different originated cancer cells. We further demonstrated that the surface tailoring of nanoparticles via mixed-charge SAM can provide a facile method to present better “stealth” properties and higher accumulation in tumor than PEG-2000 modified nanoparticles. Combing with the pH-responsive properties of weak electrolytes, the mixed charge bionanointerface can be explored as a robust method to control the aggregation of NPs sensitive to enhance the retention and cellular uptake of inorganic NPs in tumors, which has perfect stealth properties and pH-sensitivity for tumor targeting and photothermal treatment.

**COLL 453**

**Direct cytosolic delivery of siRNA using nanoparticle-stabilized nanocapsules**

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An efficient delivery of small interfering RNA (siRNA) into the cytosol of target cells remains as a challenge to the clinical translation of RNA interference (RNAi). Here, we report the use of nanoparticle-stabilized nanocapsules (NPSC) for direct cytosolic delivery of siRNA. In this approach, siRNA is complexed with cationic arginine-functionalized gold nanoparticles, with the resulting ensemble self-assembles onto the surface of fatty acid nanodroplets to form NPSC/siRNA nanocomplex. The complex rapidly and efficiently delivers siRNA into cytosol in a cell plasma cholesterol-dependent manner, in which siRNA is believed to enter cells via a route of membrane fusion. With a short half-life destabilized green fluorescent protein (deGFP) as a model gene to target, the NPSC/si_deGFP nanocomplex silenced the gene expression of deGFP stable-expressing HEK293 cells up to 90%. Moreover, the delivery of siRNA targeting polo-like kinase 1 (PLK1) silenced PLK1 expression in cancer cells with concomitant cytotoxicity. The highly efficient and effective siRNA delivery highlights the advantages of NPSC-facilitated direct cytosolic siRNA delivery as a powerful tool for in RNAi and promising platforms for biomedical delivery.
Figure 1. NPSC mediated siRNA delivery. a) NPSC/siRNA components and proposed mechanism of cytosolic siRNA delivery. b) Efficient knockdown of deGFP using NPSC/sideGFP with 40nM siRNA concentration after 48 h delivery. Scale bars: 20 μm. c) Cell viability of MDA-MB-231 cells treated with NPSC/siPLK1 or scrambled siRNA (40 nm) after 48 h delivery.

COLL 454

Pulsed magnetic field induced fast drug release from magneto liposomes via ultrasound generation

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Fast drug delivery is very important to utilize drug molecules that are short lived under physiological conditions. Techniques that can release model molecules under physiological conditions could play an important role to discover the pharmacokinetics of short lived substances in the body. Here an experimental method is developed for the fast release of the liposomes' payload without a significant increase in (local) temperatures. This goal is achieved by using short magnetic pulses to disrupt the lipid bilayer of liposomes loaded with magnetic nanoparticles. The drug release has been tested by two independent assays. The first assay relies on the AC impedance measurements of MgSO₄ released from the magnetic liposomes. The second standard permeability assay is based on the increase of the fluorescence signal from 5(6)-Carboxyfluorescein dye when it the dye is released from the magneto liposomes. The efficiency of drug release ranges from a few percent to up to 40% in case of the MgSO₄. The experiments also indicate that the magnetic nanoparticle generate ultrasound, which is assumed to have a role in the release of the model drugs from the magneto liposomes.

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Multifunctional drug carriers with programmable properties

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In nature, the hierarchical organization of material has led to the creation of unique entities that range from individual cellular components to entire organisms. Within a single mammalian cell, for example, the distinctive compartmentalization of chemical and biological functions in separate organelles has resulted in the evolution and development of eukaryotic cells in comparison to less advanced prokaryotic life forms.¹ Inspired by this organization and resultant complexity, our lab has been able to fabricate multicompartamental colloids using the electrohydrodynamic co-jetting technique. In these colloids, the internal and external architecture of the colloids can be precisely controlled to incorporate different materials and unique properties. To date, our lab has focused on the design and engineering of the internal structure to include stimuli responsive polymers, therapeutics, imaging agents, catalyzer, as well as other functional materials.² Herein we demonstrate the selective surface decoration of particles composed of three distinct regions using bio-orthogonal surface modifications, as well as the design of colloids with programmable physical properties such different shapes, sizes, and degradation kinetics.³ Such colloids with unique geometries and functionalities have implications in several fields including drug delivery, tissue
engineering, and self-assembly, a few of which will be discussed.

References:


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Multichannel nanosensor for instantaneous readout of cancer drug mechanisms

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Characterizing drug mechanism is critical in personalized medicine, where the choice of cellular pathway targeted dictates efficacy towards specific tumor geno/phenotypes. Traditional approaches require multi-step processing of cells prior to analyses and specialized equipment, limiting their applications in drug screening. A profiling method that relies on fewer phenotypes, has less time consuming steps, and readily available equipment would greatly facilitate the use of cell signature approaches for drug mechanism screening. Here, we present a high-throughput multichannel sensor platform that can profile the mechanisms of various chemotherapeutic drugs in minutes. The sensor consists of a gold nanoparticle complexed with three different fluorescent proteins that can sense drug-induced physicochemical changes on cell surfaces. In the presence of cells, fluorescent proteins are rapidly displaced from the gold nanoparticle surface due to competitive binding of the cells, leading to the restoration of fluorescence. Depending on the drug-induced cell surface changes, different patterns of fluorescence response from different fluorescent proteins can be used to identify specific mechanisms of cell death induced by drugs. The nanosensor is generalizable to different cell types and does not require processing steps before analysis, offering an effective way to expedite research in drug discovery, toxicology and cell-based sensing.
Structural and biological characterization of Fe₃O₄-loaded spherical and tubular liposomes for magnetic drug targeting

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Magnetic drug targeting (MDT) using iron-oxide-based liposomes (magnetic liposomes) have the advantage of being nontoxic and biocompatible and can provide selective delivery to tumours regardless of their type by using an external magnetic field. Spherical micelles and spherical liposomes have been used to evaluate the important
parameters for MDT (the concentration and type of ferro fluid employed, the magnetic strength of the external magnetic field, and the exposure time of the target tissue to the external magnet field). However, detailed data on the other geometries of magnetic liposomes have not been reported. Therefore, we focused on the relationship between the structures of the magnetic liposomes and their biological functions.

We characterized two different geometries of magnetic liposomes composed mostly of 1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine, DC8,9PC and L-a-phosphatidylcholine, dioleoyl, DOPC using transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS) analysis. The magnetic liposomes containing DC8,9PC were tubular in structure, and many Fe3O4 particles were present in the internal water phase. In contrast, the magnetic liposomes containing DOPC were spherical in structure, and a single particle or two particles were estimated to be present in the water phase. Subsequently, the influence of an external magnetic field and the structure of the liposomes on cellular uptake were investigated. The external magnetic field increased cellular uptake independent of the structure both in vitro and in vivo (Fig. 1). Although the amount of in vitro cellular uptake for the tubular liposomes was higher compared to the spherical liposomes, there was little difference between the influence of tubular and spherical structures on in vivo uptake in the mouse liver. Finally, the magnetic liposomes were found to be biocompatible based on haematology and serum chemistry analysis.

![IVIS imaging of livers, kidneys, and spleens of mice treated with control or magnetic liposomes (a; tubular liposomes, b; spherical liposomes) with or without the implantation of an external magnetic field.](image)

Fig.1 IVIS imaging of livers, kidneys, and spleens of mice treated with control or magnetic liposomes (a; tubular liposomes, b; spherical liposomes) with or without the implantation of an external magnetic field.

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Functionalized Nanomaterials (NMs) were produced via a green colloidal synthesis under moderate conditions. These NMs include nano-metal, nano-oxides and nano-frameworks, which were functionalized using various natural products through a post-modification approach. The use of water-soluble natural products, such as Salvia hispanica, traditional Chinese and Indian medicine, coffee and tea offer a variety of water-soluble components to enhance the reduction of noble metal aimed to increase the fluorescent intensity of those NMs in a cancer theranostics. The NMs were characterized to determine their crystalline phase structure, particle size and distribution.

The cytotoxicity on Chinese hamster ovary (CHO) cells, human ovarian cancer cells and retinal pigment epithelial cells showed these NMs possessed high potency to kill cancer cells. An effective dose at 50% of 20 ppb (cytotoxicity at 100 ppm) indicating that drug-formulated Fe$_3$O$_4$ based MNs with amphiprotic functionalization would facilitate targeting of tumour cells as demonstrated in vitro by the 3-[4,5-dimethylthiazol-2-yl]-2,5 diphenyl tetrazolium bromide) assay.

The bioassay of nitrogen monoxide (NO) release by RPE showed high fluorescence after addition of nitrite, which facilitates investigation of intracellular NO concentrations. It was also found that 4,5-diaminofluorescein diacetate analog was used to bind to NO and form a benzotriazole compounds. The bioassay of reactive oxygen species (ROS) indicated 5-(and-6)-Carboxy-2,7-dichlorofluorescein diacetate, succinimidyl ester is a useful fluorescent tracer. It can passively diffuse into cells and covalently label intracellular proteins resulting in long-term cell labeling. The reagent itself is colorless and nonfluorescent but becomes brightly green fluorescent once it is hydrolyzed by intracellular esterases.
Bioassay of nitrogen monoxide release by REP cells

**COLL 459**

**Controlled cross-linking of nano- and micromaterials for biomedical applications**

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One of the main foci of current nanotechnology research is chemical functionalization and size-control of nanomaterials. Previous research has shown that applications of a
nanomaterial are strongly dependent on its size, morphology, and surface functionality. We continue to explore various biological applications of nanomaterials. Polymeric N-halamine emulsion, a known antimicrobial material in paints, was reproducibly synthesized and polymerized with monitoring of size and surface charge throughout the process. The size control of such polymers is important because of the sensitivity of the process to various parameters. We have shown that controlled cross-linking of polymerizing particles play a critical role in the processes of seeding and successful polymerization. Cross-linking of non-toxic biopolymers inside human dentin is a perspective approach for the controlled occlusion of dental tubules critical for treating teeth hypersensitivity and constructing a scaffold for the further remineralization of teeth. We have shown that cross linking of alginate by chitosan nanoparticles or calcium ions are perspective candidates for the development of novel proactive dentifrices. The synthesized particles have been characterized by Dynamic Light Scattering, SEM, and TEM.

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Gold nanorods indirectly promote migration of metastatic human breast cancer cells in 3D cultures

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Gold nanorods are being studied widely for applications in human disease detection, diagnosis and therapy. As the field learns more about how to safely use these nanoparticles safely and with real-world success, most studies still overlook the importance of the extracellular matrix (ECM). Gold nanorods in the body will inevitably come into contact with the ECM, and fully understanding its role in the short- and long-term safety of gold nanoparticles is crucial. In order to study how these nanomaterials can influence ECM properties and cell-ECM interactions, we have created a nested gel type I collagen matrix for measuring how gold nanorods alter the migration of MDA-MB-231 human breast cancer cells in three-dimensional environments. In contrast to the few studies of gold nanorod-induced migration changes in two-dimensional environments, our results show that gold nanorods in a model ECM increase the frequency of spontaneous cellular migration. The presence of negatively-charged polyelectrolyte-coated gold nanorods during the collagen self-assembly process was shown to induce mechanical and structural changes and alter molecular diffusion, and to affect cellular adhesion, morphology, locomotion strategy and protease expression. Taken together, the characterization of collagen and cell properties after migration through these ECM models suggests that these gold nanorods may induce a mesenchymal-to-amoeboid-like migratory phenotype switch via changes to the matrix structure as a method for increased migration.

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Quantitative detection of rapid nuclear protein trafficking using nanoparticle stabilized capsules

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Delivery of proteins to cells typically results in endosomal entrapment, limiting the utility of these strategies for both fundamental and therapeutic applications. We recently developed a method for cytosolic delivery of protein using nanoparticle stabilized capsules (NPSC). NPSCs are stabilized by supramolecular guanidine-carboxylate interactions between the HKRK-functionalized gold nanoparticles (HKRK-NPs) of the shell and the hydrophobic fatty acid (oil) components in the core. This method produces a capsule that is capable of rapidly releasing active protein directly into the cytosol. We have used this method to quantitatively monitor nuclear protein trafficking. For these studies we used five different nuclear localization signals (NLS) attached to eGFP. Quantitative comparison of the nuclear accumulation of the five NLS-eGFPs from laser LSCM results showed vastly different nuclear import efficiencies. The dynamics of the nuclear accumulation of the NLS-eGFP in the cell were tracked through live cell microscopic imaging, with reached in as little as 6 minutes.

Fig.1. (a) Cytosolic delivery and nuclear accumulation of eGFP with NLSs using NPSCs. (b) LSCM image showing cellular distribution pattern of NLS-tagged eGFP. (c) Statistical analysis revealing nuclear importing efficiency (6 cells per group).
Design of molecular gelator – solvent systems guided by solubility parameters

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Molecular gels have gained tremendous attention over the past decades for their potential applications in multiple disciplines, ranging from recovery of oil spills, to serving as vehicles for controlled drug release, to structuring edible oils. Despite the vast and rapidly growing body of literature devoted to these gels, the gelation of low molecular weight compounds is still an empirical science and the majority of new structural types are discovered serendipitously. It remains difficult to predict a priori the structure of a potential gelator or to foresee the solvents that can be gelled by a known gelator. Challenges in designing these hierarchical architectures lies in the contrasting parameters, including those that promote epitaxial growth and limit solubility, mitigating the construction of complex, supramolecular nanostructures that spontaneously produce ordered ensembles of the molecular building blocks.

Although the gelator-gelator interactions are of paramount importance in understanding gelation, the solvent-gelator specific (i.e., H-bonding) and nonspecific (dipole-dipole, dipole-induced and instantaneous dipole induced forces) intermolecular interactions are equally important. Solvent properties mediate the self-assembly of molecular gelators into their self-assembled fibrillar networks. Solvatochromic parameters such as $E_T(30)$ parameters, and Kamlet-Taft parameters ($\beta$, $\alpha$ and $\pi$), are correlated with the gelation ability of numerous classes of molecular gelators. Advanced solvent clustering techniques have lead to the development of a priori tools that can identify the solvents that will be gelled and not gelled by molecular gelators. These tools will greatly aid in the development of novel gelators without solely relying on serendipitous discoveries.

COLL 463

Quantifying tension effects on phase transitions and domain features in phospholipid membranes

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Phase transitions in phospholipid membranes provide insight into the physics of phase separation in two dimensions and form the basis for structure-function relationships in biological membranes. An example of the latter is phospholipid rafts, related to signaling and trafficking. A primary focus of decades of study on these phase transitions has been the impact of temperature and composition in model vesicle membranes; however, tension has been largely neglected, in part due to the challenge of measuring and controlling it. We argue here, however, that tension can have a profound impact on membrane phase transitions, suppressing domain formation, or shifting the nature of the domains themselves. While Clausius-Clapeyron predicts depression of a melting
transition as small as 1/3 C for every mN/m of applied tension, the presence of a triple point or similar features for fluid-solid membrane transitions involving polymorphic solid phases can lead to the formation of different domains altogether. These ideas are developed in this talk in the context of the DPPC/DOPC model membrane system, where tension is thought to quantitatively influence the areal density in solid domains having tilt or corrugated molecular arrangements. Indeed, with tension demonstrated to select between the two solid polymorphs, the impact of tension on the vesicle domain morphology, for instance stripes or hexagonal phases, with different micron-scale connectivity, is profound.

**COLL 464**

**Effect of membrane composition and protein lipidation on the free energy of binding of HIV-1 matrix to lipid membranes**

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The retroviral polyprotein Gag is the single essential component required for the formation of new HIV-1 viral particles. It is initially expressed in the cellular cytoplasm but eventually targets the surface of the plasma membrane (PM) where viral assembly occurs. The N-terminal matrix (MA) domain of Gag is the key structural motif that mediates targeting. Several biochemical mechanisms are implicated in MA-membrane binding including electrostatic interactions between a patch of basic residues and anionic lipids, a hydrophobic interaction with a myristolated amino acid group and specific binding to phophatidylinositol 4,5-bisphosphate PI(4,5)P₂ found only in the PM. With a set of comprehensive binding measurements using surface plasmon resonance spectroscopy, we were able to separately quantify those individual contributions to the free energy of binding. We found that two contributions are sufficient to stably anchor MA to the membrane and that individual contributions add in a non-linear way to the total free energy of binding. Structural data on membrane-bound MA obtained from neutron reflectometry in support of the free energy calculations are presented.

**COLL 465**

**Monitoring the formation of Gram-positive bacterial membrane mimics using QCM-D**

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Although supported lipid bilayer (SLBs) composed of zwitterionic lipids and zwitterionic-anionic lipid mixtures have been used extensively to mimic eukaryotic and Gram-negative bacterial cell membranes, attempts to form supported bilayers composed entirely of anionic lipids have been less successful. SLBs fully composed of anionic lipids are valuable models for Gram-positive bacterial membranes that can be used to study the membrane interactions of particles such as antimicrobial peptides (AMPs) or nanoparticles. We developed a novel method of forming robust anionic lipid bilayers containing 3:2 and 4:1 L-α-phosphatidylglycerol (PG) and 1-palmitoyl-2-hydroxy-sn-glycero-3-phospho-(1’-rac-glycerol) (LPG) lipid mixtures, which were supported on (3-aminopropyl)trimethoxysilane (APTMS)-coated silica. Quartz crystal microbalance with dissipation monitoring (QCM-D) was used to monitor the formation of the supported bilayers by measuring nano-scale mass changes on a sensor surface as anionic lipids vesicles attached and ruptured into a bilayer. Supported PG vesicle layers were also formed to enable experiments that monitor the behavior of anionic vesicles. These supported anionic lipid bilayers can be valuable tools for studying the behavior of Gram-positive bacterial membranes in the development of antimicrobial agents or therapeutics.

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Association of model neurotransmitters with lipid bilayer membranes

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The conventional model of synaptic transmission between neurons is based on the specific binding of neurotransmitters to ligand-gated ion channels. Fast profusion electrophysiological studies of receptor responses to neurotransmitters have revealed complex kinetic behavior that cannot be reproduced unless the standard model is expanded to include a number of additional conformational states. If one invokes neurotransmitter adsorption to the lipid membrane, the electrophysiological data may be reproduced with a simpler kinetic model that includes only the standard set of three conformational states [1]. This putative indirect mechanism of influence of neurotransmitters on receptor conformational transitions is assumed to be nonspecific, i.e., a wide range of molecules, including neurotransmitters and anesthetics associate with the bilayer and affect receptor activity. Experimental verification of neurotransmitter-bilayer interactions has been difficult because of the low binding affinities of the neurotransmitters to a lipid bilayer membrane [2]. We quantify this interaction with surface-sensitive techniques including surface plasmon resonance.
(SPR) spectroscopy and neutron reflectometry (NR) on artificial membranes. Sparsely-tethered bilayer lipid membranes (stBLMs) composed of zwitterionic (PC) and anionic (PS and PG) lipids were assembled and their interactions with serotonin and γ-aminobutyric acid (GABA) were studied as model systems. SPR shows a range of binding affinities for different neurotransmitters. Consistent with these results, NR shows that the ligand with the largest affinity (serotonin) penetrates the membrane deeply whereas GABA, for which the affinity is an order of magnitude less than that of serotonin, associates with the bilayer peripherally. Overall, we establish that some neurotransmitters interact non-specifically with the lipidic membrane matrix at physiologically relevant concentrations and that this interaction differs vastly for different neurotransmitters. These results could have a significant impact on our understanding of the molecular mechanism of synaptic transmission.


**COLL 467**

Scattering and simulation studies identify molecular control mechanisms in cell signaling

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*Pten* encodes a lipid phosphatase specific for PI(3,4,5)P₃ and is one of the most frequently mutated genes in human cancers. Although PTEN acts on its substrate at the inner surface of the plasma membrane, the protein resides in the cytosol and interacts with the PM only sporadically. Homozygous PTEN loss is embryonically lethal, but heterozygous mutations show a complex spectrum of pathologies in which subtle variations in PTEN dose determine cancer susceptibility. The resulting continuous spectrum of cancer predilection is not consistent with the classical two-hit paradigm for mutations of tumor suppressor genes. To explain this intriguing finding, it was postulated that the functional form of PTEN is an oligomer in which wild-type PTEN monomers could be inactivated by mutant protein (Berger *et al.*, *Nature* 2011). Indeed, such oligomers have recently been observed in vivo (Papa *et al.*, *Cell* 2014). Here, we study structural aspects of PTEN oligomerization in vitro. PTEN comprises an N-terminal phosphatase domain and a C-terminal C2 domain that binds to anionic membranes. In addition, a short N-terminus and a long C-terminus, both disordered, have regulatory functions. A truncated PTEN core that encompasses the C2 and phosphatase domains but lacks ≈20% of the full-length protein provided a partial crystal
structure (Lee et al., Cell 1999). From SAXS data of PTEN solutions eluted from a size-exclusion column at different concentrations, we deconvolve two distinct scattering centers, find that their sizes correspond to a PTEN monomer and dimer, and observe that the dimer is favored over the monomer in buffer. Docking studies based on the truncated PTEN crystal structure revealed four candidates for a dimer complex, all with approximate C2 symmetry, that expose the membrane binding interfaces of both monomers, known from prior neutron reflection studies of PTEN on artificial membranes (Shenoy et al., J. Struct. Biol. 2012), on the same interface. MD simulations currently in progress explore the putative full-length PTEN dimer structure and dynamics, and investigate the roles of the disordered protein stretches in dimer stabilization.

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Modeling interactions between charged nanoparticles and multicomponent vesicles

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We develop a computational model to design and characterize multi-component vesicles interacting with functionalized and charged nanoparticles using the Molecular Dynamics simulation technique. Our aim is to generate a stable vesicle through the self-assembly of amphiphilic lipid molecules via the use of implicit solvent coarse-grained molecular models in order to investigate biologically important physiological processes occurring on the mesoscopic spatio-temporal scales. The amphiphilic lipid molecules are represented by a hydrophilic head group and two hydrophobic tails. In addition, we use two component lipid mixtures to study the formation of hybrid lipid vesicles through the self-assembly. We find that the degree of phase segregation between the two lipid species is tunable via their distinct effective chemical specificity and molecular architecture [1]. Furthermore, we have extended the model to introduce the charged lipid molecules into the vesicle by using long-range electrostatic interactions between charged molecules. We investigate the interactions of various functionalized nanoparticles with the charged lipid species and effects of these interactions on the dynamics and morphologies of the lipid vesicles. Our findings can be used to design new soft biomaterials for various applications in medicine, sensing and energy.


COLL 469

Direct probes of supported lipid bilayers interacting with 4-nm diameter gold nanoparticles

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This work presents molecular-level investigations of how well-characterized silica-supported phospholipid lipid bilayers formed from either pure DOPC or a 9:1 mixture of DOPC:DOTAP interact with positively and negatively charged 4-nm sized gold metal nanoparticles at pH 7.4 and NaCl concentration ranging from 0.001 to 0.1M. Second harmonic generation (SHG) charge-screening measurements indicate the supported bilayers carry a negative interfacial potential. Resonantly enhanced SHG measurements probing electronic transitions within the gold core of the nanoparticles show the particles interact largely irreversibly with the supported bilayers at concentrations. At 0.1 M NaCl concentration, surface coverages for the particles functionalized with the negatively charged ligand mercaptopropionic acid (MPA) or wrapped in the cationic polyelectrolyte poly(allylamine) hydrochloride (PAH) are estimated from a joint analysis of QCM-D, XPS, AFM, and ToF-SIMS to be roughly 1 x 10^7 and 1 x 10^11 particles cm^-2, respectively. Results from complementary SHG charge screening experiments point to the possibility that the surface coverage of the MPA-coated particles is much more limited by interparticle Coulomb repulsion due to the charges within their hydrodynamic volumes than the surface coverage of the PAH-wrapped particles. Yet, SHG adsorption isotherms indicate that the interaction strength per particle is largely independent of ionic strength and particle coating, highlighting the importance of multivalent interactions. ^1H NMR spectra of the lipids within vesicles suspended in solution show little change upon interaction with either particle type, but indicate loosening of the gold-bound PAH polymer wrapping upon attachment to the vesicles. The thermodynamic, spectroscopic, and electrostatic data presented here may serve to benchmark experimental and computational studies of nanoparticle attachment processes at the nano-bio interface.

COLL 470

Interphase effects on polymer and water dynamics in cellulose biocomposites – ^2H and ^13C NMR relaxometry

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Improving the control of moisture stability and interface structures in plant fiber biocomposites is a key challenge in the design of novel cellulose nanocomposites with suitable mechanical performance as packaging materials and as hydrated plant cell wall analogues. In order to clarify detailed nanostructural effects in water/biocomposite systems, a unique approach based on ^2H and ^13C NMR relaxometry is presented here where the molecular dynamics of adsorbed water and of polysaccharides are for the first time characterized separately. These two sensitive NMR methods were successfully combined and applied to core-shell and more inhomogeneous nanocomposites from cellulose nanofibers (CNF) in xyloglucan (XG) biopolymer matrix to assess hydration effects in ^4H_2O atmosphere.
In the neat XG and CNF components, $^2$H transverse relaxation ($T_2$) data were consistent with water clustering at the CNF fibril surfaces, but bulk spread of moisture in XG. At low hydration, water molecules at the CNF/XG interface exhibit higher water mobility than in neat CNF or XG, due to the locally high water concentration. At the same time, CNF-associated interphase segments of XG show more constrained NMR-dynamics than in neat XG. The results clarify the molecular and nanostructural details of the composites (interface and interphase phenomena) and explain their mechanical stability under moist conditions.

COLL 471

Quantitative tissue spectroscopy of near infrared fluorescent nanosensor implants

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Implantable, near infrared (nIR) fluorescent nanosensors are advantageous for in vivo monitoring of biological analytes since they can be rendered selective for particular target molecule while utilizing their unique optical properties and the nIR tissue transparency window for information transfer without an internal power source or telemetry$^1$. However, basic questions remain regarding the optimal encapsulation platform, geometrical properties, and concentration ranges required for effective signal to noise ratio through biological tissue. In this work, we systematically explore these variables quantitatively to optimize the performance of such optical nanosensors for biomedical applications$^2$. We investigate both alginate and polyethylene glycol (PEG) as model hydrogel systems, encapsulating d(GT)$_{15}$ ssDNA-wrapped single walled carbon nanotubes (SWNT) as model fluorescent nanoparticle sensors, responsive to riboflavin$^3$. Hydrogel sensors implanted 0.5 mm into thick tissue samples cause 50% reduction of initial fluorescence intensity, allowing an optical detection limit of 5.4 mm and 5.1 mm depth in tissue for alginate and PEG gels, respectively, at a SWNT concentration of 10 mg L$^{-1}$, and 785 nm laser excitation of 80 mW and 30 s exposure. These findings are supported with in vivo nIR fluorescent imaging of SWNT hydrogels implanted subcutaneously in mice. For the case of SWNT, we find that the alginate system is preferable in terms of emission intensity, sensor response, rheological properties, and shelf life.

Facile assembly enhanced spontaneous fluorescent response of Ag$^+$ containing polyelectrolyte multilayer films

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Fluorescent organic–inorganic composite materials exhibiting “turn-on” response are often based on conjugated small molecules. Conjugated polymers, however, often exhibit a “turn-off” response in combination with metal ions. Here we present fluorescent turn-on behavior of a branched poly(ethylene imine)-poly(acrylic acid)-Ag$^+$ ion complex in a thin film. The material is characterized by UV-vis, spectrofluorometry, XPS, and ICP-MS. The turn-on response is exhibited only with all three components present, implying that the optically active metal coordination complex contains amine and carboxylic acid groups. This behavior is observed in the solid state, meaning this material could be easily integrated into devices. We demonstrate sensing of formaldehyde vapor as well as halide containing solutions based on fluorescence quenching. This fluorescent material is simply made using the layer-by-layer technique and commercially available polymers.

Characterizing polymeric micelles employed for DDS by use of SAXS and FFF
Polymeric micelles have been extensively studied as nano-scale drug carriers. The studies of the micellar inner-structures that encapsulate hydrophobic drugs is important to design effective carrier. Poly(ethylene glycol)-block-poly(partially benzyl-esterified aspartic acid) is one of the most studied systems from both synthesis and biological aspects. However, little is known about fundamental physical properties. We synthesized various samples with different compositions and characterized them with field flow fractionation (FFF) and synchrotron small-angle X-ray scattering (SAXS).

We found that the major factor to determine the micellar structures and the aggregation number is the benzylation rate of the core block: hydrophobicity of the core. By knowing the aggregation number and the core size, we can determine how the tethered PEG chains are overcrowding. We are first to quantitatively correlate the PEG-chain crowdedness and biological activity of the micelles.

We also used as hydrophobic compound tetrabromocathecol (TBC) as a drug-equivalent model molecule. The bromine atoms in TBC act as probes in anomalous small-angle X-ray scattering (ASAXS) allowing for its localization in the polymeric micelles. We found that the radius of the spherical region populated with bromine atoms was larger than the one of the sphere corresponding to the hydrophobic core of the micelle. This result suggests that the TBC molecules infiltrate the PEG hydrophilic domain in the vicinity of the core/shell interface.
Controlling nanocomposite hydrogel mechanics via bioinspired interfacial bond dynamics

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Dynamic interactions between polymer molecules and inorganic nanoparticle surfaces can play a critical role in bulk mechanical properties of soft nanocomposite materials. However, controlling such interfacial interactions remains a significant challenge. Inspired by the adhesive chemistry in mussel threads, we present a novel approach to control soft composite mechanics via polymer-particle interfacial dynamics; by incorporating iron oxide nanoparticles (Fe$_3$O$_4$ NPs) into a catechol-modified polymer network the resulting hydrogels are crosslinked via reversible metal-coordination bonds at Fe$_3$O$_4$ NP surfaces thereby providing a dynamic gel network with robust self-healing properties. By studying the coupling between composite network mechanics and polymer-NP binding dynamics we have found that material properties can be engineered from both sides of the metal-organic interface. This early demonstration of control over nanocomposite hydrogel mechanics via bio-inspired interfacial bond dynamics offers an expansive platform for future design of soft nanocomposite materials.
Micromechanical properties of nanostructured soft silicon hydrogel contact lenses

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Introduction of silicone hydrogel materials drew close attention to the mechanical properties of soft contact lenses, in particular due to the necessity of lens modification for hydrophilicity and the ocular complications associated with the use of less compliant materials. In this work we present a method for micromechanical characterization of several commercially available soft silicone hydrogel contact lenses, which allows examination of spatial variation of mechanical properties within the lens. In this study we employ modulus calculation through simple elastic contact mechanics models applied to force-distance curves collected from nanoindentation experiments performed with AFM. Such experiments give moduli values independent of the sample shape and size. The measurements were performed on the lens cross section to map the mechanical properties distribution within the bulk of the lens. In addition we have studied topography and mechanical properties of the lens surfaces, which come to the direct contact with the eye tissue. Resulting AFM images show high contrast distribution maps for the adhesive and mechanical properties of the microstructured regions such as pores, lamellae and different material inclusions within the lenses. Additional indentation experiments allow tagging of these different contrast regions with precise values of elastic moduli.

**COLL 476**

Nanostructured functional thin films through vapor phase deposition: A BIMREL’s approach to bioinspiration

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The ability to control the physicochemical properties of surfaces is important for many areas such as biomedical or optical coatings, sensors, and catalyst supports. We have been developing nanostructured polymeric and metallic thin films based on oblique angle deposition (OAP) method for these applications without using any lithography techniques or template materials. These films possess novel anisotropic (directional) properties which could be potentially manipulated based on the growth conditions and the deposition parameters. The surface-to-volume ratio of structured films is very high and the available surface area increases by more than two orders of magnitude in relation to the bulk film. We are studying nucleation, crystallinity and growth as well as pore size and geometries of nanostructured thin films. Our technique opens a new wealth of applications to assemble many possible combinations of monomers or metallic precursors that have desired functional groups or plasmonic features for creating novel
thin films. In this presentation, we will describe our process for creating nanostructured thin films and present results concerning their applications.

COLL 477

Design of multistimuli responsive films through LbL assembly for the control of protein adsorption

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Control of protein-material interactions plays a key role in numerous biomedical fields, such as tissue engineering, drug delivery, proteins separation. In this regard, the emergence of smart polymers that reversibly respond to environmental stimuli has opened new routes for control of surface properties, particularly, the behavior of proteins at the solid-liquid interface.

In the current study we report on the design of multi-stimuli responsive thin films. For this purpose, we employed the layer-by-layer (LbL) assembly approach to incorporate block copolymers made of poly(acrylic acid) PAA and poly(N-isopropylacrylamide) PNIPAM with tunable and well-defined block lengths. The combination of ellipsometry, quartz crystal microbalance (QCM) and infrared data revealed the possibility to build up (PAH/PAA-PNIPAM)ₙ multilayers.

Stimuli-responsive properties of LbL films were examined by monitoring the proteins adsorption by means of QCM and fluorescence measurements, while varying (i) temperature, (ii) pH, (iii) ionic strength, or (iv) a combination of above parameters. It discloses that temperature has a strong impact on amount of adsorbed proteins, in agreement with the expected behavior of PNIPAM. In addition to the successful design of stimuli-responsive films, the mechanism of protein adsorption is deeply investigated, as it looks to be more complex, compared to tests performed on “common” flat surfaces. This is due to the fact that physicochemical changes influence, at the same time, the properties of LbL films, done with weak polyelectrolytes. Indeed, protein adsorbed amount estimated by fluorometry measurements suggests that various processes may occur at the interface: protein accumulation on top and/or penetration within the films, depending on pH and ionic strength of solution.

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Remote giant multispectral plasmonic shifts of labile hinged nanorod array via magnetic field

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Color-based sensors have shown great promise in their ability to function as inexpensive and easily interpretable detection platforms. These changes in color often result from chemical reactions in the sensor device, leading to a one-time use application. Recently, it has been shown that coupling plasmonic and responsive materials together can lead to drastic, reversible changes in color. In this light, we report a remotely mediated and fast responsive plasmonic–magnetic nanorod array with extremely large variability in optical appearance (up to 100 nm shifts in scattering maxima) and concurrently for multiple wavelengths in a broad range from visible to near-infrared (at 450, 550, and 670 nm) with an external magnetic field with variable direction. The remotely controlled system suggested here is a magnetic field-directed assembly of an ordered monolayer array of unipolar oriented magnetic–plasmonic nickel–gold nanorods flexibly hinged to a sticky substrate. The unique geometry of the mobile nanorod array allows for the instant alteration of the surface plasmon polariton modes in the gold segment of the controllably tilting nanorods. This design demonstrates the utility of hybrid bimetallic nanoparticles and gives a novel approach to the design of fast-acting, remotely controlled color-changing nanomaterials.
Much attention has been paid in recent years to the improvement of the durability of highly transparent superhydrophobic surfaces. In this report, superhydrophobic surfaces are fabricated using three steps. First, chemical and morphological changes are generated in the polyester mesh by alkaline treatment. Second, alkaline treatment causes hydrophobic molecules of perfluorodecyltrichlorosilane (PFDTS) to react with the hydroxyl groups on the fiber surfaces. Third, hydrophobicity is enhanced by treating the mesh with SiO₂ nanoparticles modified with PFDTS using a spray method. The transmittance of the fabricated superhydrophobic mesh is approximately 80 % in the visible range. The water contact angle and the water sliding angle remain greater than 150 ° and lower than 25 °, respectively, and the transmittance remains approximately 79 % after 100 cycles of abrasion under approximately 10 kPa of pressure. The mesh surface exhibits a good resistance to acidic and basic solutions over a wide range of pH value (pH 2–14) and the surface can also be used as an oil/water separation material because of its mesh structure. It was found that the fabricated mesh maintains its superhydrophobicity and low water sliding angle because of the surface treatment, although the nanoparticles modified with PFOTS are removed by the abrasion. Therefore, compared with the traditional technology, the combination of the see-through mesh and the nanoparticle hierarchical structure is an effective and simple method for improving the abrasion resistance and transparency of these superhydrophobic films. This simple but novel and effective method may be useful for the improvement of highly transparent superhydrophobic surfaces for various applications.

The overall objective of our research is to determine the degree of surface deposition resultant from the aerosolization of a solid or dusty material. Current methods for measuring the amount of deposited material require extraction of material from the surface, a process which involves manipulations that can disturb the settled material. In order to facilitate more reliable measurements of the amount of aerosol deposited, we have developed a model system of silica nanospheres, of known size and shape, with a lanthanide element incorporated into the spheres. The lanthanides we have chosen to work with are europium, terbium, and samarium, elements whose fluorescence spectra are well characterized. Addition of the lanthanides to the silica nanospheres allows fluorescence surface sampling to be performed after deposition, permitting measurement of the material without risk of disturbance or dislodging due to movement during traditional surface sampling techniques. Preliminary measurements of the 200 nm Eu-doped spheres have shown the fluorescence intensity to be linear ($R = 0.9998$) over 0.1 µM to 100 µM concentrations of the doped spheres in IPA. Results have also indicated that detection of the spheres is more sensitive for surface sampling, than in solution. Use of multiple lanthanides allows for different doping for specific particle sizes. Based on particle size distribution data collected for agent aerosols, several different sizes of the lanthanide doped spheres can be mixed together to represent an
aerosolized threat, with respect to the deposition hazard. Data collected from such experiments can be used in current hazard prediction models.

**COLL 481**

**Facile synthesis and surface modification of HfO₂ nanoparticles for nanocomposite γ-ray scintillators**

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Inorganic nanoparticles/polymer nanocomposites provide a low cost, high performance alternative for gamma scintillation. However, inorganic nanoparticles used thus far suffer from either moderate atomic numbers or low band gaps, limiting the gamma stopping power and photoelectron production in these systems. Here we report a facile single-precursor synthesis protocol for hafnium oxide nanoparticles with uniform size distribution and excellent solubility in non-polar solvents. The nanoparticle surface was further functionalized for the fabrication of bulk-size transparent nanocomposite monoliths. Using poly(vinyltoluene) as the matrix, 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole and 1,4-bis(5-phenyl-2-oxazolyl)benzene as the cascade fluors, and hafnium oxide nanoparticles as the gamma sensitizer, the nanocomposite monolith of 1 cm diameter and 2 mm thickness was fabricated capable of producing a full energy photopeak for 662 keV gamma rays.

**COLL 482**

**Hydrophobic mesoporous silica discoids for effective sorption of oil substances**

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We have recently reported the self-assembly of ordered mesoporous silica discoids by acid catalyzed condensation of sodium silicate in presence of cetyltrimethylammonium bromide surfactant. Here we demonstrate a modification those particles to make them efficient sorbents of oil (nonpolar) substances, which can be used for decontamination and cleaning of aqueous phase. These, ~3 mm sized particles have uniform cylindrical pore channels concentric to their rotation axis. N₂ adsorption studies yield average pore diameter of 2.9 nm, surface area of 1160 m²/g and a total pore volume, 0.84 cm³/g. The silica surface is hydrophobized through surface modification and co-condensation approaches, for oil adsorption. The absorption studies using a water emulsion of ASTM D5307 Crude oil internal standard indicates that complete pore filling occurs after oil absorption. This would amount to a total crude oil absorbing capacity of 40% of discoid weight (>80% by volume). Thermogravimetry show that the removal of absorbed oil
occurs in a continuous single step. Up to 93% of the adsorbed oil is removed by 90°C heating in vacuum within 24 h. The high absorption capacity and cheaper inorganic precursor source make these particles promising for large scale decontamination and cleaning applications.

**COLL 483**

**Ultrabright fluorescent silica particles for multiplexing security tagging and labeling**

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Here we report on ultrabright fluorescent micron-size silica particles for multiplexing tagging and labeling which can be used in security applications. Fluorescence of these nanoporous (mesoporous) silica particles comes from fluorescent molecules physically encapsulated inside of the particle’s pores. A special molecular design prevents the dye molecules from leaking from the pores. This technology allows encapsulating multiple dyes in different proportions simultaneously. As a result, one can obtain complex spectra, which can be used as a sort of “UPC color barcode” for tagging and labeling of various items, materials, and products. Because of close proximity of the dye molecules, they can effectively be used in the FRET regime. This further adds to complexity of the spectra because it can now be excited with a broader range of wavelengths. We also investigate the question of how many different spectra can be obtained with this technology. Our estimation shows that the number of different spectra produced within this technology is virtually unlimited (billions of combinations), and thus, is restricted by technical requirements of specific applications.

**COLL 484**

**Self-assembly of quantum rods into controlled alignments using DNA origami and their use as energy acceptors in bioluminescence resonance energy transfer**

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Our lab is interested in harnessing both the energy accepting, as well as the polarization properties of CdSe/CdS quantum rods. In particular, we are interested in using self-assembly to organize rods with controlled spacing and orientations, the result of which will determine the optical response. By using DNA-mediated interactions, we recently described a route to assemble rods with controlled spacing and geometry onto DNA origami (*Nanoscale* 2015, 7, 2883). In this presentation we will describe the approach, recent advances, and new ultracentrifugation routes to purify the assemblies. We use these rod+origami assemblies as novel substrates upon which to probe the energy
accepting properties of the rods. For this, we build on our recent studies that show bioluminescence resonance energy transfer (BRET) is particularly efficient between Photinus pyralis (Ppy) firefly luciferase and quantum rods (Nano Letters, 2012, 12, 3251) and that multi-step BRET-FRET using QRs is possible (Nanoscale 2013, 5, 5303). In this presentation we will describe recent experiments designed to use these organized rods to study BRET, as well as describe recent studies focused on understanding the origins of the high energy transfer efficiency. Potential defense applications will be discussed, including our recent work using quantum rod BRET for near-infrared emission and signaling (Nanotechnology, 2014, 25, 495606). We thank the AFOSR for support of this work (FA9550-10-1-0033).

COLL 485

Effect of capping agent on the interactions of zinc sulfide nanocrystals with a model environmental surface

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The adsorption of ZnS nanoparticles capped with different materials was investigated on the model environmental surface of the iron oxyhydroxide goethite using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Nanoparticles were prepared with the amino acids histidine, phenylalanine, serine, and cysteine as capping agents, as well the polymer poly(vinylpyrrolidone), or PVP. Size characterization revealed that all of the nanoparticle samples were in the 3 to 4 nm size range. Results of the adsorption studies were fitted to a first order kinetic rate model and from this model relevant rate constants were determined for the adsorption processes. First order treatment revealed a significant difference in adsorption dynamics amongst the capping agents used. In some instances two rate constants resulted from the fitting of the data. Nanoparticles capped with amino acids containing hydrophilic side groups (histidine, serine and cysteine) underwent formation of a multilayer. The sole hydrophobic amino acid, phenylalanine, and the hydrophobic PVP showed only monolayer association with the goethite. The results and experiments found in this work represent a novel investigation of a fundamental process in the environmental chemistry of ZnS nanoparticles.

COLL 486

Direct views of the nano-bio interface

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The interaction of a well-characterized set of ligand-coated nanoparticles with lipid bilayers of varying chemical composition is described for conditions in which ionic strength and pH are controlled. Nanoparticle- and membrane-specific data obtained
from microscopy, spectroscopy, scanning probe, coarse-grain computational, and mass measurements show that gold and diamond nanoparticles with 4 and 15 nm core diameters alter zwitterionic lipid bilayers under conditions of 100 mM NaCl when they are coated with the common cationic polyelectrolyte poly(allylamine hydrochloride). Other particle-ligand combinations surveyed leave the bilayers intact. Free ligand controls point to a 100-fold increase in the local cationic polymer concentration when wrapped around the nanoparticle core as a molecular rationale for the observations. We hypothesize that bilayer disruption coincides with lipid corona formation around the particles. Implications for nanoparticle-induced effects observed at the single- and multicellular organism levels are discussed.

COLL 487

Influence of a combined lecithin and Pluronic F127 surfactant on stability of lutein-loaded zein nanoparticles as a function of time and temperature

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Physical-chemical stability of lutein, known as naturally occurring antioxidant carotenoid due to its ability to quench singlet oxygen, is the main drawbacks for its application in food and pharmaceuticals. To take full advantage of its potential as an antioxidant, a protein-based nanoparticle approach is proposed as a way to provide bioactive protection during manufacturing production and on-shelf storage. In this research, lutein-loaded zein nanoparticles, made with and without surfactants were synthesized using a solvent-free liquid-liquid dispersion method. A combination of phospholipid soybean lecithin and tri-block copolymer Pluronic F127 was used in the formulation as surfactants to promote its physicochemical stability. Physical stability of zein nanoparticles was investigated at 4°C, 25°C, and 40°C by measuring size, polydispersity index (PDI), and zeta potential. Chemical stability of entrapped lutein was assessed in parallel, by measuring the absorbance using a UV/Vis spectrophotometer at 445 nm and emulsified lutein were studied as a control. The results showed that zein nanoparticles with surfactants were stable at low temperature, measuring between 156.1±18 to 380.8±51 nm when stored at 4°C for 30 days. At temperature ≥ 25°C, particles without surfactants were less stable after 7 days. No significant differences were found in changes of nanoparticle polydispersity and zeta potential values over time. Surfactants not only provided long-term storage stability, but also delayed the degradation. Only 26% of entrapped lutein in the presence of surfactant system was degraded after 30 days at 25°C, compared to 54% degraded in the system without surfactants at the same time. In the absence of nanocarrier, emulsified lutein degraded faster at all temperatures. Based on these stability data in terms of characteristics of the particles and lutein concentration over time, it is apparent that with the addition of surfactants to protect lutein against degradation, zein nanoparticles provide a promising way to enhance its function for various food and health applications.

COLL 488
Effect of humic acid and fulvic acid on the aggregation and stability of TiO$_2$ nanoparticles

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Natural organic matter (NOM) and ionic strength (IS) influence the aggregation of titanium dioxide nanoparticles (TiO$_2$ NPs). In the aqueous environments, Humic acid (HA) and Fulvic acid (FA) are typical NOM. Therefore, it is necessary to study the adsorption of HA and FA onto the TiO$_2$ NPs under different IS and its impact on the aggregation of TiO$_2$ NPs. In this study, time-resolved hydrodynamic size of the TiO$_2$ NPs was measured to calculate the attachment efficiency and critical coagulation concentration (CCC) of TiO$_2$ NPs. Our results showed that FA is easier than HA to reach the CCC of TiO$_2$ NPs due to their different molecular weight and functional groups. The existence of HA promotes the aggregation of TiO$_2$ NPs when ionic strength is higher than CCC, while FA doesn’t promote it in the same condition (10 mg/L TiO$_2$ NPs, HA=10 mg/L, FA=10 mg/L, CaCl$_2$=30 mmol/L, pH=8). When ionic strength is higher than CCC, HA was found to have more effect on TiO$_2$ NPs aggregation than FA. It may be due to the fact that the bridging effect of HA with TiO$_2$ NPs is stronger than FA under the same pH and IS. HA contains more highly conjugated structure and higher relative molecular weight than FA. This leads to higher hydrophobic properties of HA compared with FA, and HA is easier to transfer from water phase to the surface of TiO$_2$ NPs. AFM images indicated the different spatial forms of HA and FA absorbed onto the surface of the TiO$_2$ NPs. The adsorption layer of HA is thicker and more rough than that of FA. Compared to FA, HA contains more long chain alkanes. FA molecule is smaller, and it mainly contains carbohydrate and polysaccharide. The difference of HA and FA structure results in various behavior of the aggregation and stability of TiO$_2$ NPs in aqueous phase.

COLL 489

Enhanced NOM removal from drinking water sources using stable dispersions of poly(vinylbenzyl trimethylammonium chloride) functionalized SWCNTs synthesized under ARGET-ATRP conditions: "Nano-resins" for water purification

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Dissolved organic carbon (DOC) and natural organic matter (NOM) in public water is a source of a potential health hazard, and is difficult to remove. Modern water treatment methods rely on the use of chlorine as a disinfectant to remove bacteria. However, certain DOCs (humic and fulvic acids) will react with chlorine to form chlorinated disinfectant byproducts (DBPs), which are known carcinogens. The EPA lists the maximum contaminant level for DBPs in the range of 0.01-1.0 mg/L. At such low concentrations, it is very difficult to remove these DOCs before the chlorination process.
We have synthesized “nano-resins” by covalently attaching poly(vinylbenzyl trimethylammonium chloride to Single-Walled Carbon Nanotubes (SWCNTs), which acts as an anion exchange resin, for removal of these contaminants. Polymer was grown via an FDA approved method known as Activators Regenerated by Electron Transfer (ARGET) Atom Transfer Radical Polymerization (ATRP), and attached to the SWCNTs using the same catalyst. Functionalized SWCNTs were then characterized using Raman Spectroscopy, IR, and SEM. Raman data showed a significant increase in D:G band ratio over pristine SWCNTs indicating covalent bonding to the nanotubes. Additionally, SEM images showed conformal coating of the polymer around the nanotubes. Dissolved organic carbon can be extracted from water sources by adsorption to these polymer chains on the functionalized SWCNTs. These nano-resins are stable in water, and can be recycled and then reused through addition of NaCl. This is a sustainable solution to a difficult environmental problem. Work has also been completed to optimize the polymer chain length for enhanced DOC adsorption. We have characterized the use of these functionalized SWCNTs through the adsorption of a surrogate dye from water and from marine samples in local aquifers using UV-Vis and TOC analysis. Significant decreases in contaminant concentration were observed, even at very low concentrations. Adsorption studies show that our functionalized SWCNTs are three times more efficient than currently available removal technologies and are capable of removing DOCs well below the limits set by the EPA; Langmuir adsorption studies confirm this, and show a significantly higher adsorbent saturation capability.

COLL 490

Stabilization of lipase (CaLB) through hierarchical interfacial assembly and performance in deep eutectic solvents

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Enzymes enable high specificity in production of value-added agricultural products, but are limited by challenges in stability and recovery. Hierarchical systems that integrate nano- and macroscale structural elements offer increased stability over traditional immobilization methods by reducing desorption and increasing retained activity. Hierarchically ordered particles were synthesized using interfacial assembly of lipase B from Candida antarctica and iron oxide nanoparticles onto the surface of crosslinked polydicyclopentadiene spheres, yielding ~10 micron microparticles. We have evaluated the impact of this hierarchical ordering on the stabilization of lipase (CaLB) and characterized the stability of the hierarchical assembly in greener solvent systems. Performance of the lipase microparticles in environmentally friendly solvents was characterized using two deep eutectic solvents: choline chloride and urea (ChCl:U, 1:2), and choline chloride and glycerol (ChCl:Gly, 1:2). Following exposure to deep eutectic
Evidence for the use of nanoparticles for improving crop productivity

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Nanomaterials (nanoparticles; NPs) possess small size and, thus, large surface area, which confers them with superior reactivity over larger-sized (bulk or micro) particles of similar chemistry. These characteristics of NPs have led to their use in a variety of applications. For example, zinc oxide NPs are in heavy use in personal care products such as sunscreen, cosmetics, textile, paintings, industrial coatings, dye-sensitized solar cells, antibacterial agents and optic and electronic materials. Many of the metal oxide NPs are bioactive in plant systems, the exact outcome dependent on the dose applied. This potentiates their use for beneficial purposes in agriculture. Studies of NPs in plant systems have demonstrated that nanotechnology can be leveraged in developing crop production products to enhance agricultural productivity. For instance, in wheat, ZnO NPs cause the stimulation of lateral roots and change the root architecture, which could contribute in the uptake of nutrients. In cluster bean (Cyamopsis tetragonoloba), a low dose (10 mg/kg) of ZnO NPs stimulated shoot growth, similar to findings in chickpea and green pea. At relevant concentrations, iron oxide (magnetite/hematite [Fe₃O₄/Fe₂O₃]) and Mn NPs have shown beneficial effects on plants through the stimulation of chlorophyll production or the enhancement of the rate of photosynthesis. Iron oxide NPs also could reduce the severity of chlorosis in plants. Other NPs synthesized from non-mineral nutrients have also demonstrated positive effects on plants. Work with spinach reported improved physiological and growth responses to TiO₂ NPs, wherein increases in rubisco activase activity and chlorophyll production are thought to result in enhanced photosynthesis, consequently stimulating spinach growth. Metal oxide NPs such as ZnO, Mn and CuO also play a role in disease suppression because they are toxic to plant pathogenic microbes. Collectively, the application of NPs in crops permit high uptake of the cognate element into the plant, helping to improve crop nutrition, growth and yield, while providing an opportunity for the plant to survive pathogen infections. Given current findings, it is anticipated that in the near future, the crop nutrition and protection industries will join in the nanotechnology revolution. This presentation highlights evidence of the potential for NPs to be used for improving crop performance.
Light management using nanophotonic organic materials

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Nanoscale optical wave guides, modulators, resonators, and lasers are important components of miniaturized nano-photonics devices. In particular, one dimensional (1D) organic solids are promising candidates to manipulate, guide and store optical waves down to nano/submicro/micro domains. Based on the type of light a 1D solid propagates, organic optical wave guides can be classified into active- and passive-waveguides. In 2012, Our group has discovered for the first time the passive wave guiding tendency of organic solids. We have observed that the weak Raman interaction of the propagating light with the tube molecular building blocks can also be used to pin-point nano/micro scale defect sites inherited during the self assembly process. Further more we have developed laser cutting techniques to cut the longitudinal dimension of 1D organic solids, thereby precisely control the light propagation distance down to submicro scale. Recently, we performed successful experiments to delaying the propagating light within the organic rod waveguides for all optical switching applications. Our group also developing nano/micro scale light emitting polymer micro resonators displaying “Whispering Gallery Modes (WGM)” with high Q-factors for applications such as laser sources, filters and all-optical switches.

The use of cellulose nanocrystals (CNCs) in optical materials has been extensively described in literature. Key in most applications reported to date is the chiral nematic ordering present in CNCs. Here, we demonstrate that random packing of surface modified CNCs can also yield materials with interesting optical properties, i.e. quarter-wave antireflective coatings (ARCs).

To date, two groups reported the use of CNCs in ARCs: Podsiadlo et al. reported the manufacturing of ARCs through layer-by-layer deposition of poly(ethylene imine) and CNC.\textsuperscript{1} To realize a coating thickness in the quarter-wave regime for visible light (approx. 100 nm thickness), they deposited 12 or more bilayers. The lowest refractive index achieved in their study was 1.28. Qi et al. reported a similar approach, resulting in systems with 11 or more bilayers and a lowest refractive index of 1.41.\textsuperscript{2} Although both systems are of interest from a proof of concept point of view, they are of limited practical use. They require 22 or more deposition steps, the layer-by-layer systems are
mechanically fragile, difficult to combine with prototypical binder systems and coating additives for wet-chemical formulations and have a refractive index higher than ideal (for a glass substrate with refractive index 1.50, the ideal refractive index of the ARC is 1.22).

Here, we present the development of a quarter-wave ARC based on silicated CNCs. We present the preparation of CNCs from Avicel within the specifications required for optical coatings. Furthermore, we report the synthesis of well-defined CNC-silica core-shell particles and the application of these particles in quarter-wave ARCs. Through random packing, the CNC-silica core-shell particles yield a highly porous coating of quarter wave thickness in one single dip coating step. The lowest refractive index achieved was 1.08. The silicated CNCs are compatible with prototypical coating additives, and the resulting porous layers allow addition of binder to increase the mechanical robustness, without increasing the reflection. Additionally, we demonstrate that the CNCs can be removed through pyrolysis resulting in a layer of hollow silica nanorods. This can be applied to further lower the refractive index of the film.


COLL 494

Optical gain engineering in colloidal quantum dot solids toward continuous wave lasing

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To date, lasing in colloidal quantum dot solids has been limited to the nanosecond temporal regime, and chief cause of nanosecond-only operation has been thermal runaway: the combination of rapid heat injection from the pump source, poor heat removal, and a highly temperature-dependent threshold. Herein, we represent a systematic work on lowering the optical threshold and improving the heat dissipation to overcome thermal issue, and our quasi-continuous-wave lasing result. Firstly, we study the effect of shell thickness in CdSe-CdS colloidal quantum dots on optical gain and amplified spontaneous emission and find unexpectedly higher thresholds for the thickest-shell samples. Facilitated by the ultra-fast transient absorption measurement with intentional core-only pumping, we decoupled the effects of absorption cross-section and Auger lifetime, and discovered that inhomogeneous broadening counteracts the population inversion at a given wavelength, increasing in such a way the amount of excitons per dot required to achieve optical gain on a femtosecond timescale. At nanosecond timescale, this leads to acceleration rather than deceleration of Auger recombination in thick-shell colloidal quantum dots. Secondly, based on above discovery, we selected core-shell quantum dots with medium
shell thickness and depressed inhomogeneity for further optimization. We show microsecond-sustained lasing, achieved by placing ultra-compact colloidal quantum dot films on a thermally-conductive substrate, the combination of which minimizes the amplified spontaneous emission threshold. Specifically, we employ inorganic-halide capped quantum dots that exhibit high modal gain (1250 cm⁻¹) and an ultra-low amplified spontaneous emission threshold (peak power of ~50 kW/cm²) and rely on an optical structure that dissipates heat while offering minimal modal loss. We conclude with a discussion of the path to continuous-wave lasing and light amplification from colloidal quantum dot solids.

**COLL 495**

**Effects of V doping and MCM-41 loading strategies on the fabrication of Ti³⁺-TiO₂ quantum dots and its photocatalytic applications**

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Nanosized TiO₂, especially quantum dots (QDs), generally show better performance than the bulk materials because of the highly dispersed photoactive sites and effective separation of photoinduced charges. We fabricated V-doped TiO₂ quantum dots (QDs) with Ti³⁺ defects by hydrolysis method using doping and support loading strategies. It was found that QDs are highly dispersed on MCM-41 surface without any aggregations, and Ti³⁺ defects and V⁴⁺ dopants lead to new band levels near the conduction band of QDs and show more effective charge separation. The QDs show high charge-separation efficiency and high photocatalytic activity in degradation of organic dyes and isomerization of norbornadiene due, due to the quantum size effect and the newly formed defect- and dopant-mediated band levels.

**COLL 496**

**Iron chalchogenide nanocolloids for spray-printed solar cells**

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Currently there are no reports of Fe₂Si₅ and Fe₂Ge₅ nanomaterials-based solar devices, despite their almost ideal direct bandgap of ~1.55 and ~1.4 eV (for Fe₂Si₅ and Fe₂Ge₅ respectively). Due to <0.1μm required thickness, as anticipated by the extinction coefficient >10⁵ cm⁻¹, these materials hold theoretical solar cell efficiency potential comparable with current materials (~20%) . The new ultra-thin-film technology showed in this presentation offers an alternative to
other solution-processed materials from abundant elements, such as CZTS which requires numerous layers to build the absorber layer (at least 5 to 8, as reported by research groups at Solexant, IBM and DuPont). We demonstrate that the desired 100 nm thickness necessary to accomplish defect-free, polycrystalline layers of Fe$_2$SiS$_4$ / Fe$_2$GeS$_4$ could be achieved by a simple spray process of solution precursors, followed by a flash-annealing step. The fabricated solar devices will be presented.

**COLL 497**

**Sol-gel chemistry of self-assembled photonic crystals**

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Self-assembly provides a simple, bottom-up approach to making nanomaterials with great scientific and technological interest stemming from the unique phenomena that can occur at this length-scale. One example of a self-assembled nanostructure is the inverse opal, an ordered, porous material formed from the negative space in a colloidal crystal. Due to its high periodicity, it is a three-dimensional photonic crystal, giving it interesting optical properties. Due to its high porosity, it forms a regular, interconnected network, giving it interesting wetting properties. In combination, the order and porosity allow inverse opals to be used in a variety of applications ranging from catalysis to pigments; however, precise control over the composition and morphology of the structure is necessary to achieve additional functionalities.

In this talk, I will describe how sol-gel chemistry can be used to gain molecular control over the morphology and composition of inverse opals, thus affecting macroscopic properties. In particular, we use the degree of condensation of the sol-gel precursor to control the morphology of the pores [1], achieving anisotropic inverse opals based on condensation-induced shrinking perpendicular to the substrate. This change in morphology alters the periodicity of the structure, leading to a shift in the optical spectrum [1]; additionally, the anisotropic pore shape causes liquids to fill the structure from one direction preferentially [2]. Finally, we investigate using sol-gel chemistry to control the composition of the matrix in order to adjust the refractive index, and hence tune the optical spectrum. We find that sol-gel chemistry provides a convenient handle over the morphology and composition of inverse opals to control the optical and wetting properties.


**COLL 498**

**Photocatalytic reduction of fumarate to succinate on ZnS mineral surfaces**
The reductive tricarboxylic acid (rTCA) cycle has been proposed as an autocatalytic cycle capable of starting prebiotic metabolism before the appearance of enzymes. Recent work demonstrated that ZnS could serve as a model photocatalyst to lead three out of five reductions of the rTCA cycle. The conversion of oxaloacetate to malate, fumarate to succinate, and 2-oxoglutarate to oxosuccinate were accomplished with 75 %, 95 %, and 2.5 % efficiency, respectively. However, the mechanism of these photocatalytic reactions remains unknown, demanding an explanation that could provide clues to overcome the negative results for the conversion of succinate to 2-oxoglutarate and oxalosuccinate to isocitrate. In this work we explore the mechanism for the photoreduction of fumarate to succinate on irradiated ZnS in the presence of Na2S hole scavenger. The characterization of synthesized ZnS nanoparticles was performed by XRD, TEM, EDS, Raman microscopy, and photoluminescence spectroscopy. Dynamic light scattering shows the aggregation of colloidal particles with sizes 40-220 nm at pH ≥ 6.0, and the isoelectric point at pH = 4.2. The rate of succinate production ($R_S$) decreases linearly with increasing wavelengths of irradiation ($\lambda$): $R_S (\mu\text{M/min}) = 3.8792 - 0.01118 \times \lambda$ (nm). The reaction rate depends on pH as the fraction of available monodissociated fumaric acid, indicating this species is the primary electron acceptor. The apparent quantum yield of succinate production ($\Phi_S$) under irradiation at $\lambda \geq 305$ nm is 0.47 %. We will report experiments showing that electron transfer on the conduction band and valence band hole loss during the photoreduction occur in the timescale of milliseconds. These results provide new understanding to advance the field of photocatalysis as a driver of important prebiotic reactions.

**COLL 499**

**Enhanced photoreduction of nitro-aromatic compounds by hydrated electrons derived from indole on natural montmorillonite**

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A new photoreduction pathway for nitro-aromatic compounds (NACs), and the underlying degradation mechanism are described. 1,3-Dinitrobenzene was reduced to 3-nitroaniline by the widely distributed aromatic molecule indole; the reaction is facilitated by montmorillonite clay mineral under both simulated and natural sunlight irradiation. The novel chemical reaction is strongly affected by the type of exchangeable cation present on montmorillonite. The photoreduction reaction is initiated by the adsorption of 1,3-dinitrobenzene and indole in clay interlayers. Under light irradiation, the excited indole molecule generates a hydrated electron and the indole radical cation. The structural negative charge of montmorillonite plausibly stabilizes the radical cation hence preventing charge recombination. This promotes the release of reactive hydrated electrons for further reductive reactions. Similar results were observed for the photoreduction of nitrobenzene. *In situ* irradiation time-resolved electron paramagnetic resonance and Fourier transform infrared spectroscopies provided direct evidence for
the generation of hydrated electrons and the indole radical cations, which supported the proposed degradation mechanism. In the photoreduction process, the role of clay mineral is to both enhance the generation of hydrated electrons, and to provide a constrained reaction environment in the galley regions, which increases the probability of contact between NACs and hydrated electrons.

**COLL 500**

**Enhanced multiwavelength upconversion through excitation energy trapping in NaErF₄ core-shell nanocrystals**

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Lanthanide-doped nanocrystals’ unique ability to upconvert multiple low-energy (near infrared, NIR) photons to a high-energy (UV or visible) photon, as well as their lack of blinking and high photostability, suggest that they could revolutionize bioimaging, photovoltaics, and displays. Recent efforts have focused on enhancing the upconversion efficiency of these nanostructures, while simultaneously broadening the possible excitation wavelengths. In particular, epitaxial growth of a minimally mismatched shell has proven highly beneficial to enhance upconversion efficiency. The epitaxial layer also enables integration of different sensitizers (for example, Nd³⁺ for 800 nm) spatially separated at different layers for excitation wavelength tuning. However, efforts to date have not permitted increasing the activator (emitter) ion concentration (~ 2%) due to the increase in concentration quenching at higher activator concentration. We have addressed both the excitation wavelength tuning and increasing the activator ion concentration within a single upconversion platform. Heavily erbium-doped core nanocrystals are almost optically silent under NIR excitation as the excitation energy migrates to the surface. However, after epitaxial shell growth, we observe that the excitation energy can be effectively trapped within the core, allowing for enhanced upconversion emission both under 980 and 800 nm. Our preliminary results show high upconversion quantum yield for these structures, and ongoing work is focused on the studying the excited state lifetime to understand the effects of erbium concentration and shell growth.
Coll 501

Efficient tailoring of upconversion selectivity by engineering local structure of lanthanide nanocrystals

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Lanthanide doped upconversion nanocrystals gain extensive attention due to their unique and fascinating spectral characters. With low phonon energy, fluoride based compounds are efficient supporters for upconversion emissions. However, upconversion emissions from lanthanide doped fluoride nanocrystals are fixed in wavelengths because of the invariant energy levels of lanthanides. On this basis, efficient tailoring of upconversion selectivity is thus of great important for multicolor imaging and displaying applications.\(^1\)

Here, we develop a facile and highly effective method to tailor the upconversion selectivity by engineering the local structure of lanthanides in fluoride nanocrystals.\(^2\) The lattice parameter, as well as coordination number and local symmetry of lanthanides are found to be directly related to the upconversion selectivity (Figure 1). For example, the red to green emission ratio of Er\(^3+\) varied from 1.9 to 71, 1.6 to 116 for NaxYF\(_{3+x}\):Yb,Er and NaxGdF\(_{3+x}\):Yb,Er nanocrystals, respectively. It is also noteworthy that the overall emission intensity of Er\(^3+\) increases with the engineering of local structure, and further enhances by 400 times with an epitaxial CaF\(_2\) nanoshells, which greatly promises in vivo imaging.
Lighting-up carbon nanotubes: Decorating carbon nanotubes with asymmetrical cyanine dyes

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Imparting new optical features such as enhanced light absorption and fluorescence emission to carbon nanotubes is desired for their visualization in biological applications as well as utilization as photoactive hybrid materials. Herein we studied interactions of asymmetrical cyanine dyes with carbon nanotubes to obtain highly light absorbing and fluorescent nanohybrid materials. Inspired by the light-up behavior of asymmetrical cyanine dyes upon intercalation into nucleic acids, we hypothesized that DNA wrapped carbon nanotubes can act as optimal scaffolds on which asymmetrical cyanine dyes can bind with increased quantum yields leading to light emitting carbon nanotubes. Single stranded DNA, carbon nanotubes and asymmetrical cyanine dyes were shown to self assemble into nanohybrids which can absorb and emit light in the ranges of the spectrum where carbon nanotubes alone cannot. Resulting nanohybrids were characterized for their binding stoichiometry and thermal stability by utilizing absorbance and fluorescence spectroscopy; furthermore, their fluorescence was visualized with confocal microscopy. This work constitutes the first example where fluorophores light up upon binding to carbon nanotubes as opposed to being quenched, thus provides a novel approach for both fluorescent labeling of carbon nanotubes and utilization of carbon nanotubes as photoactive materials.
Single stranded DNA, asymmetrical cyanine dyes and carbon nanotubes self assemble into fluorescent nanohybrids.

**COLL 503**

**Investigation of the stability of silver halide films on the atomic scale**

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In a recent publication, it was suggested that a AgCl film on a metal surface afforded extreme resistance to both thermal and oxidative damage while remaining atomically ordered and free of contamination. The film was formed on a Au(111) crystal through the use of under potential deposition (UPD) of Ag in the presence of chloride. UPD is a useful procedure as it allows for the controllable and reproducible deposition of up to a few atomic layers of a metal before the onset of bulk deposition. Unexpectedly, the film remained intact on the surface after heating cycles as high as 1,000 K and subsequently became even more structurally ordered than the original film. The atomic structure of these films is studied with electrochemical scanning tunneling microscopy (EC-STM). This technique 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 are used to examine the redox behavior of the systems. Despite many studies on these types of surface layers, very few publications have directly studied their extreme thermal stability. Since it is known that the stability of bulk metal halide structures decreases as the halogen ion increases in size, the stability of 2D AgBr or AgI films is examined and compared to what has been determined for the AgCl film. These atomically thin and ultra-stable films may find applications in a variety
of fields from self-assembly and sensing to select anti-corrosion applications.


COLL 504

Oxygen deficient surfaces in metal oxide nanopowders

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Metal oxides are of broad importance in materials applications ranging from catalysis to thermal barrier coatings to semiconductors and insulators to bioceramic implants to fuel cells. Decades of careful characterization of surface structure, energetics, and reactivity has provided a detailed picture of surface processes for single crystals and thin films of key oxides. Use of metal oxides in nanopowder form is increasingly common. Given technological relevance is often associated with surface properties more than bulk, the modifications of these in nanoscale oxides is of fundamental importance. At the same time, electron spectroscopy and microscopy methods are less applicable in these powders exhibiting low crystallinity. We discuss our recent alumina nanopowder studies employing nuclear reaction analysis coupled with density functional calculations (Vykhodets et al. Surf. Sci. 2014 630 182) suggesting surface structure similar to that in the (√31×√31)R9° reconstruction of α-Al2O3 (0001) as well as current studies involving additional metal oxides.

COLL 505

Semiconducting group IV quantum dots for tunable bandgaps

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Advances in photonic materials are commonly made through thin film deposition production of new materials. These methods are commonly limited by availability of epitaxial substrates. One rising material that faces such issues is Ge1-xSnx, the instability of the alloy requires that films be strongly bound to substrate. However, such epitaxial has been shown to prevent the transition from an indirect to direct bandgap, a driving force behind this materials development. To remove epitaxy from the equation we have developed a colloidal strategy to produce uninhibited Ge1-xSnx alloys. We report the synthesis of phase pure Ge1-xSnx alloy nanocrystals (NCs) as solid solutions with a wide range of sizes from ~3 nm to ~25 nm and compositions from x = 0.00-0.28. The larger Ge1-xSnx nano-alloys (15-23 nm) provide a strong foundation for determining the crystal properties. Solid state absorption spectra indicate near infrared bandgaps 15-23 nm Ge1-xSnx NCs suggesting a minimum size quantization. In contrast, the smaller Ge1-xSnx NCs (3.0 - 6.0 nm) exhibit composition tunable bandgaps that are
significantly blue shifted from corresponding bulk counterparts. Ge$_{1-x}$Sn$_x$ NCs both dried and colloidally dispersed were characterized utilizing, XRD, XPS, TEM, STEM, Raman, Uv-Vis and IR, spectroscopy. Additionally, Tauc analysis was used to explore the changes in optical bandgaps with the NCs demonstrating composition tunable indirect and energy gaps from 1.31-0.75 eV and direct energy gaps from 1.47-0.95 eV for $x = 0.00-0.16$. To improve the quality of surface passivation and elucidate luminescent properties, ZnSe and CdS were selected as coating materials. Development of the coating procedure and the effects on the luminescent intensities will be focused on.

COLL 506

Surface chemistry of metal oxide nanoparticles

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Understanding the surface chemistry of nanoparticles is vital to many fields, including clean energy production and storage, heterogeneous catalysis, materials chemistry, and environmental remediation. Nanoparticles are significantly more reactive than larger substrates due to their increased surface to volume ratio; however the structural and electronic effects of nanoparticles do not necessarily mimic the macroscopic properties of the bulk material. In addition, studying the surface interactions on nanoparticles can be quite difficult due to the “materials gap”, where the material used is not well-defined or characterized, and the “pressure gap”, where the substrates are exposed to ambient conditions and reactions are performed either at high pressures or even in the liquid phase. This project describes recent work focused on the surface chemistry of metal oxide nanoparticles, such as TiO$_2$, ZnO, and ZrO$_2$, commonly used in catalytic systems. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is well suited for analyzing the surface reactions on semiconducting nanoparticles. These particles are mostly transparent to the infrared and the multi-bounce nature of the diffuse reflectance helps to increase the signal from these low coverage reactions. Atomic Force Microscopy is useful to monitor changes in nanoparticle morphology over the course of complex reactions. Confocal Raman Spectroscopy allows for the determination of structural variability, especially in the case of TiO$_2$ which has different Raman spectra for the rutile and anatase phases. Together all of these tools have been used to monitor reactions and analyze product formation between the nanoparticles, both commercially available and synthesized, to a variety of probe molecules, such as acetic acid, formic acid, water and methanol, under a variety of different exposure conditions, predominantly gas exposure but also including liquid exposure.

COLL 507

Structural evolution in Ag-Ag$_2$S hybrid nanoprisms during sulfidation

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Recently Ag-Ag₂S hybrid nanostructures have attracted a great deal of attention due to their enhanced chemical and thermal stability and also their morphology and composition dependent tunable local surface plasmon resonance. It has been shown that these Ag-Ag₂S nanostructures can be synthesized via the sulfidation of as-prepared Ag anisotropic nanoparticles. Yet, this process is poorly understood, often leading to anomalous syntheses and unaccountable physical properties. In this work we use theory and experiment to investigate the structural and plasmonic evolution of Ag-Ag₂S nanoprisms during the sulfidation of Ag precursors. The previously observed red-shifted extinction of the Ag-Ag₂S hybrid nanopism as sulfidation occurs is in contradiction to theoretical predictions, indicating that reaction doesn’t just involve the prism tips as previously speculated.

Our experiments demonstrate that sulfidation can induce either blue or red-shifts in the extinction of the dipole plasmon mode depending on reaction conditions. By elucidating the correlation between the final structure and morphology of the synthesized Ag-Ag₂S nanoprisms, we find that depending on the reaction conditions sulfidation occurs on both the prism tips and the (111) surfaces, leading to a core(Ag)-anisotropic shell(Ag₂S) prism nanostructure. Additionally, we demonstrate that, depending on the relative amounts of Ag₂S at the prism tips and Ag₂S shell thickness around the prism, the dipole plasmon can shift either way.

Scanning transmission electron microscopy, electric field distribution and extinction spectra of hybrid nanoprinism.

COLL 508

Unique adsorption behaviors of carboxylic acids at rutile TiO₂(110)
The coverage-dependent adsorption behavior of acetic acid (CH$_3$COOH) on rutile TiO$_2$(110) was investigated by means of density functional theory (DFT) calculations, corrected by on-site Coulomb corrections and long-range dispersion interactions. The p(2×1) and c(2×2) domains of dissociatively adsorbed acetic acid under different coverages have been studied in detail regarding their structural and energetic properties. Adsorptions of formic acid (HCOOH) and carbonic acid (H$_2$CO$_3$) were also considered for better understanding the adsorption behaviors of carboxylic acids. Our calculation results show that carboxylic acids prefer to dissociatively adsorb in bridging bidentate configuration, and it induces significant surface relaxation at the adsorption site, which also affects other surface atoms nearby. Interestingly, we have shown that such adsorption induced relaxations still maintain bond symmetries for surface Ti cations within the p(2×1) domain while they are drastically broken within the c(2×2) domain, giving rise to unstable Ti cations at the surface. This work not only explains the long lasting puzzle of the preferable occurrence of p(2×1) domain for the adsorbed carboxylic acids at rutile TiO$_2$(110), it also proposes a novel scheme that metal oxide surfaces may follow when they are involved in the processes like surface functionalization and self-assembly.

COLL 509

Solvent effect on CO$_2$ electrochemical reduction on Pb(211) and Sn(112)

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Pb and Sn have been widely studied as electrode catalysts for CO$_2$ reduction. The general observation is that formic acid is the dominant product with a high Faradaic yield (~90%) on both electrodes. We performed a comparative study of the electrochemical reduction of CO$_2$ on stepped Pb(211) and Sn(112) surfaces based on the results of density functional theory slab calculations. We mapped out the potential energy profiles for electrochemical reduction of CO$_2$ to formate and other possible products on both surfaces. To verify the validity of the results, we also considered the solvation effect and mapped out the reaction energetics diagram by employing the implicit solvent model. Our results show that the first step is the formation of the adsorbed formate (HCOO$^-$) species through an Eley-Rideal mechanism. The formate species can be reduced to HCOO$^-$ through a one- electron reduction in basic solution, which produces formic acid as the predominant product. The respective potentials of forming HCOO$^-$ are predicted to be -0.72V and -0.58V on Pb and Sn. Higher overpotentials make other reaction pathways accessible, leading to different products. On Sn(112), CO and CH$_4$ can be generated at -0.65V following formate formation. However, formation of other intermediates on Pb(211) is highly unlikely because a high
limiting potential (-1.33eV) would be required. All the results are consistent with that in implicit solvent model. Although solvation effect would stabilize most intermediates to some extent, it did not change the mechanism.

**COLL 510**

**Interfacial hydrogen bonding of substituted benzene derivatives on silica: The effects of electron withdrawing and donating groups**

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A fundamental understanding of the forces that drive uptake and binding of aromatic molecules on well-characterized surfaces such as silica is an important step in learning about the fate of toxic industrial compounds in the environment. These interfacial forces are also relevant to a variety of militarily relevant systems including the uptake of chemical warfare agents on metal oxides. Therefore, the adsorption of simple substituted benzene derivatives has been investigated on a hydroxyl-functionalized surface to understand the effects of electron withdrawing and donating functional groups. Specifically, this work probes how methyl and halide functional groups affect the properties of the OH---π hydrogen bond and other surface-adsorbate interactions that play an important role in the uptake of aromatic molecules. Our approach utilizes infrared spectroscopy to study hydrogen bond formation and temperature–programmed desorption to measure activation energies of desorption. Results from this work indicate that substituted benzene derivatives adsorb to silica via a cooperative effect involving the SiOH---π hydrogen bond and additional substituent-surface interactions that result in unusually high desorption energies.

**COLL 511**

**Effect of metal ions on the swelling performance of the hydrogel in enhancing salt resistance**

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Effect of metal ions on the swelling performance of the hydrogel in enhancing salt resistance.
Since polymer gels have been widely used for reservoir conformance control (flooding efficiency control) in industry, hydrogel, derived from acrylic monomers, including acrylamide (AM), acrylic acid (AA) and 2-Acryloylamino-2-methylpropane-1-sulfonic acid (AMPS) had attracted significant interest in recent years. A series of hydrogels employed these monomers and some kind of metal ions were developed for conditions conformance control in extreme salinity (>100000ppm), under which condition current gel’s swelling ratio will be limited a lot. The gels produced by this kind of crosslinking system processed a controllable swelling ratio, especially under very high salinity conditions. Metal ions, including Na(I), Ca(II), Al(III) and Cr(III), had been added into the gel network as crosslinkers and additives. Since the existence of one or some of them, an osmotic pressure system forms in gel. The internal metal ions of the gel help to neutralize external ions effects during swelling process. As a result, synergistic effect happened together with hydrogel’s spontaneous expansion to balance gels’ swelling ability. The effect of monomer concentration (1%~25%wt), pH, initiator concentration and crosslinker concentration on swelling ratio and rheological property were investigated. Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were measured. The salinity stability mechanism was discussed in this work.

COLL 512

On the intrinsic wettability of graphite

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Graphitic materials are long believed to be hydrophobic. Here we show that a clean graphitic surface is in fact mildly hydrophilic. We find that a freshly exfoliated graphite surface gave a water contact angle of ca. 64°. Upon exposure to ambient air, the water contact angle gradually increased to ca. 85° within 60 min. Infrared (IR) spectroscopy showed that airborne hydrocarbon adsorbed onto the graphite surface during this process. Both thermal annealing and controlled UV/O₃ treatment removed the hydrocarbon contaminants, which was accompanied by a concurrent decrease in the water contact angle. Our findings show that graphite is more hydrophilic than previously believed and suggest that the reported hydrophobic nature of graphite is due to unintentional hydrocarbon contamination from ambient air.

COLL 513

Charge transfer effect of bimetallic nanostructures: Tuning SERS

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Surface-enhanced Raman scattering (SERS) is a powerful tool for trace detection of molecule. The enhancement mechanism relies on local surface plasmon properties of a metal nanoparticle. An increase of the electromagnetic field near the metal nanoparticle surface has great effect on the enhancement factor. Here we present the effects of bimetallic nanostructures on SERS response. Charge transfer between two metals and hot-spot generation are the two main signal enhancement factors. In a bimetallic system, the metal with the higher Fermi level can transfer electrons to the next metal which has a lower Fermi level until the bimetallic nanostructures achieve electronic equilibrium. As a result of charge redistribution, one metal becomes partial positively charged and the other metal achieves a partial negative charge. The electromagnetic field which is generated by excitation of the surface plasmon of the metal nanoparticle will combine with this local electric field and improve the Raman signal intensity. We compare results from several bimetallic combinations and obtain an agreement between Raman intensity and the charge transfer effect. The charge transfer mechanism between metals is confirmed by work function data from Kelvin Probe Force microscopy. We test the SERS response of our materials by detecting the signal intensity of adsorbed polyaromatic hydrocarbons (PAHs), which are marked as a serious environmental pollutants. The main objective of our work is to explain the charge transfer mechanism of different bimetallic combinations and its effect on SERS signal intensity of adsorbed molecules.

References:
TMV-dendrimer bottlebrush conjugates

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Tobacco Mosaic Virus (TMV) is the most widely studied virus in the world and consists of 2130 identical protein subunits arranged helically around a single genomic RNA strand. TMV forms rodlike structure and has been covalently functionalized previously to form homogeneous and monodisperse materials with a high degree of quality control. The well-defined chemical structure of the TMV capsid can be modified internally or externally with single molecules and polymers, though attachment of dendritic substrates has not yet been demonstrated. Dendrimers are perfectly branched macromolecules with well-defined structures and are promising tools for drug delivery as they are ideally sized in vivo carriers and their multivalency, biocompatibility, and monodispersity. In this research we are combining the benefits of dendrimer chemistry with the homogeneity of TMV for use in biomedical applications and nanoelectronics. Our dendrimer functionalized TMV can be considered a bottlebrush polymer with a specific preprogrammed length, making it an anisotropic, monodispersed, and highly homogenous new material. The aliphatic polyester based family of dendrimers is used for the bio-conjugation because of their known biocompatibility and low cytotoxicity towards human cells. Moreover, the properties and interesting possible applications of this novel material will be discussed.

Diblock copolymer worm-gels for cellular immobilization and storage

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The physicochemical interaction between stem cells and the extracellular milieu is crucial for determining cell fate. Often, such cells undergo rapid proliferation once adhered to an extracellular matrix. In this respect, one of the main challenges in this area is maintaining stem cells in a non-proliferative, pluripotent state for extended periods of time (weeks rather than days). We have recently developed a wholly synthetic thermoresponsive copolymer gel comprising poly(glycerol monomethacrylate)-poly(2-hydroxypropyl methacrylate) [PGMA-PHPMA] diblock copolymer worms. These gels can be synthesized via RAFT aqueous dispersion polymerization of HPMA using a PGMA macro chain transfer agent. The growing PGMA-PHPMA diblock copolymer
chains undergo polymerization-induced self-assembly on the nanoscale to form wormlike micelles which form free-standing gels due to inter-worm contacts. These gels undergo reversible de-gelation on cooling due to a worm-to-sphere order-order transition, allowing facile sterilization for biological applications via cold ultrafiltration. In this work, we describe in detail, how the traditional RAFT aqueous dispersion polymerization system developed by our group has been adapted in order to prepare copolymers which are suitable for biological applications. In addition, we show that there is no interaction between stem cells and the material allowing them to remain in a non-proliferative state for an extended period of time.

COLL 516

Sugar-based surfactants utilizing low molecular weight, atactic poly(α-olefins) as tunable hydrophobic groups

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Synthetic designs for surfactants have historically been constrained by the limited range and availability of different types of functionalized hydrocarbon moieties that can serve as hydrophobic ‘tails’ that are chemically tethered to hydrophilic ‘head’ groups. This talk will introduce a new and highly versatile class of surfactant hydrophobe that is derived from the living coordination polymerization of α-olefins that is conducted in a manner that provides practical quantities of end-group functionalized, low molecular weight atactic poly(α-olefins) of tunable side-chain structure. In addition to possessing extremely narrow polydispersities, these non-crystalline atactic poly(α-olefins) hydrophobes are further characterized by possessing low glass transition temperatures, \( T_g \). Through the use of copper-catalyzed azide-alkyne cycloaddition ‘click’ chemistry, peracetylated monosaccharide head groups were chemically-linked to a variety of poly(α-olefins) of varying structure and number-average molecular weight values. Both peracetylated and deacylated sugar-poly(α-olefin) conjugate surfactants were characterized in the bulk solid-state, as ultra-thin films and in mixed solvents by an arsenal of techniques, including TEM, AFM, GPC, DLS, MALDI-TOF and NMR. These studies help to elucidate the various roles played by the sugar head group and the poly(α-olefin) tail in controlling self-assembly and potential utility in water cleanup and enhanced oil recovery, to name a few.

COLL 517

PEG decorated core-shell pNIPAm hierarchical microgels via host-guest interactions

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Poly(N-isopropylacrylamide) (pNIPAm) – based microgels represent one of the most studied groups of thermoresponsive materials. They are considered as auspicious candidates for various applications, ranging from scavenging of heavy metals to controlled drug delivery [1]. However, microgels of simple uniform architecture have a number of significant limitations as drug delivery vehicles, i.e. burst release of actives and fast opsonization by blood serum proteins [2]. In order to overcome these limitations, the anchoring of β-cyclodextrin groups and PEG grafts onto core-shell pNIPAm-polyacrylic acid microgels is elaborated in this work, using bi-layer surface modification with a host β-cyclodextrin polymer [3] and guest (PEG, adamantane)-grafted dextran (Fig.1).

We report the synthesis of novel bifunctional (PEG, adamantane)-grafted dextrans by copper-catalyzed azide-alkyne cycloaddition (CuAAC). Their affinities to native β-cyclodextrin and β-cyclodextrin polymers were evaluated in solution by ITC and at planar interface by SPR. Then negatively charged pNIPAm-100%AAc core-shell microgels were modified using a two-step procedure: a) Host-guest driven formation of precursor complexes between positively charged β-cyclodextrin polymer and (PEG, adamantane)-grafted dextran; b) adsorption of the precursor complexes onto microgels via electrostatic interactions. Overall charge of the obtained particles can be tuned from negative to positive, depending on βCD content, while their colloid stability and temperature responsiveness of the pNIPAm core are preserved. Due to the presence of β-cyclodextrin and PEG-containing outer shells, hierarchical pNIPAm microgels open the path towards drug nanocarriers with improved release kinetics and “stealth” properties.


Figure 1. PEG decorated pNIPAm microgel preparation strategy.
Reactive amphiphilic polymer additives for self-decontamination of CWA simulants

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Contamination of material surfaces from chemical warfare agent attack presents significant risk for extended periods of time due to the extreme toxicity and persistence of agents. Development of self-decontaminating materials, specifically polymeric coatings and fibers, affords potential to substantially mitigate the risk of surface contamination. Therefore, reactive nanoparticles, C\textsubscript{60} fullerene and a Nickel containing polyoxometalate, have been incorporated into polymeric coatings, their dispersion behavior as a functional of chemical modification were investigated, and the self-decontaminating capability of the polymer coatings against chemical warfare agent simulants were assessed. Chemical modification of the reactive molecules was performed to impart amphiphilic character to facilitate their automatic segregation to the polymer-air interface. Surface characterization utilizing SEM, XPS, contact angle, IR, and XRD was conducted. Decontamination challenges against simulants were performed in well characterized simulated daylight conditions and analyzed via GC-MS. Preliminary results of research into the compatibility of reactive nanoparticles into polymer nanofibers through electrospinning are also presented.

Chemical threat responsive carbon nanotube membranes

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Current research efforts are aimed at developing hybrid polymer-vertically aligned carbon nanotube (CNT) membranes that are breathable in their native state but become blocked upon exposure to low levels of chemical warfare agents (CWA). Our approach utilizes polymers formed by ring opening metathesis polymerization (ROMP) that have a highly non-planar structure in their neutral resting state to retain the high moisture vapor transport rate of the CNT membranes. Upon reacting with CWAs, these polymers can ionize and planarize, assuming a cationic, aromatic structure. This π-stacking drives a gel collapse that will block the CNT pores. These types of polymers will be grafted from the membrane using surface initiated ROMP (SI-ROMP) on norbornene-substituted surfaces. In this approach, the surface will be functionalized with a reactive ruthenium catalyst, and subsequent addition of norbornene-based monomers will result in a
functional polymer grown from the membrane surface. It is envisioned that this hybrid material will be useful to protect soldiers from chemical and biological threats.

COLL 520

Metal-organic frameworks for the removal of G-agents and sulfur mustard

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Over the past decade metal-organic frameworks (MOFs) have been utilized for various applications including gas storage, separations, catalysis, sensing, and toxic-gas removal. MOFs are of great interest in these areas because of their high surface areas and ability to have the inorganic and organic portions tailored to a particular application. More recently MOFs have been investigated for their reactive removal of chemical warfare agents (CWAs) and their simulants. The porosity and density of metal oxide like sites in the secondary building unit make MOFs ideal structures for the reaction of CWAs and the potential sequestration of byproducts. While most studies have been done on simulants, we present here the direct reaction of CWAs on MOFs in the presence and absence of solvent. Here we report on the reactive removal efficiency of sarin, soman, and sulfur mustard by UiO analongs and NU-1000, among other MOFs. Information about the reaction kinetics and mechanism was elucidated using nuclear magnetic resonance. Notable results include the removal of sarin by NU-1000 with a half life of approximately 3 minutes. The effects of MOF porosity and the density of reactive sites as pertaining to selection and design strategies for determining the ideal MOFs to study for CWA removal will be thoroughly discussed. MOFs can be engineered into a variety of materials including filters, fibers, and coatings to protect the warfighter.

COLL 521

Nanometric hydrogen bronze reagents for the detection and neutralization of explosives

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Explosives pose a deadly risk to our society as a consequence of intentional use by terrorists. Life threatening explosions can also result from accidental detonation resulting from mishandling of explosives, discharge of unexploded ordinance, or even build up of peroxides in otherwise safe solvents. Molybdenum and tungsten hydrogen bronze are promising materials that can react with explosives and render them non-explosive. Hydrogen bronze nanometer thick films and nanoparticles have the ability to store hydrogen in the form of hydroxyl groups attached to the reduced metal ions and
behave as reducing reagents towards the nitro or peroxide groups in common explosives. Both the color and electrical conductivity of these materials change dramatically during the course of this reaction. The nanometric materials have been shown to be effective in neutralizing military (RDX) and improvised (HMTD and TATP) explosives. Various catalytic systems are envisioned to minimize the amount of material required for neutralization

**COLL 522**

**Porous Co$_3$O$_4$ nano-array based monolithic catalysts for low temperature CO and hydrocarbon oxidation**


Monolithic catalysts constructed with porous Co$_3$O$_4$ nanowire arrays have successfully been fabricated by a facile hydrothermal method. Enabled by the nano-array configuration, the catalytic materials utilization efficiency has been greatly improved by 10-40 times compared with the traditional wash-coated monolithic catalyst. The porous Co$_3$O$_4$ nano-arrays are uniformly grown over the large cordierite substrate and foreign atoms such as Ni and Zn can be successfully doped into the lattice with controlled concentration. The Ni incorporation has been discovered to promote catalytic activity of CH$_4$ oxidation while for CO oxidation both Ni and Zn doping deteriorate the activity. Density functional theory simulation together with spectroscopy investigation demonstrates lattice oxygen is responsible for the catalytic oxidation. Operando study furthers reveals the effects of doping element upon the surface intermediate formation as well as the catalytic reaction activity.

**Reference**


a-c) Photographs of cordierite honeycomb substrates before and after porous Co3O4 nanoarray catalyst coating; d-f) SEM images of porous Co3O4 nanoarrays prepared from different precursors.
Catalytic performance of a) CH₄ oxidation and b) CO oxidation; DFT calculations to determine the c) crystal structure of doped Co₃O₄ and d) surface chemisorption behavior.

**COLL 523**

**3D ZnO/Perovskite core/shell nanorod array based catalysts: A promising PGM-free catalyst for low temperature hydrocarbons oxidation**

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Hydrocarbons, a major component in automotive exhaust emission, contribute to the serious global air pollution and the greenhouse effect. The current commercial catalytic aftertreatment systems, usually relying on washcoated powder-form catalysts, are challenged by increasingly stringent automotive emission regulation and rapid consumption of platinum-group-metal (PGM). Recently, we demonstrated that large scale ZnO/Perovskite core/shell nanorod arrays with great geometry and catalytic performance tunability could be uniformly integrated onto commercial 3-D honeycomb cordierite substrates, displaying good robustness, catalytic conversion and material utilization efficiencies. In comparison to powder-form perovskite catalyst, the core/shell nano-array based monolithic catalyst shows enhanced catalytic activity and reaction kinetics by lowering the activation energy and shifting the light-off temperature to lower temperature, which holds great promise for low temperature hydrocarbon oxidation for emission control. We develop a consecutive synthetic approach to prepare monolithic catalysts with different thickness of perovskite nanoparticle coatings and different lengths of core/shell nanorod arrays. The catalysts display a length-dependent catalytic oxidation performance upon similar LaMnO₃ loading amount. The dispersion of perovskite nanoparticles on ZnO nano-arrays with different geometry and the synergy of interfaces between perovskite and ZnO nanorod support impose important influences on the catalytic activity of ZnO/perovskite core/shell nanorod array based monolithic catalysts. Our work presents a new type of catalysts for oxidation of hydrocarbons, especially highlights a new way to enhance catalysts’ catalytic activity at low temperature. These core/shell nano-array based monolithic catalysts could be a promising PGM-free catalyst to bridge nano-catalysis with practical catalytic emission control applications.
Silver nanoparticles (AgNPs) have raised concerns over their potential threat to human health and the environment due to their increasing applications in food industry, consumer goods and agriculture. However, current analytical techniques cannot meet the requirements for probing AgNPs in various sample matrices. The objective of this study is therefore to develop an effective method for analyzing AgNPs in different types of samples by using surface-enhanced Raman spectroscopy (SERS). A crucial step of the method development is to select a best reporter that is able to produce distinct and high SERS signals and bind to the surface of AgNPs strongly. By using ferbam (ferric
dimethyl-dithiocarbamate) as the best reporter, the characteristic SERS spectrum of ferbam could indicate the presence of AgNPs. The underlying mechanism is mainly based on the localized surface plasmon resonances (LSPR) of AgNPs that induce strong electromagnetic enhancement, particularly to the molecules (e.g. ferbam) bound on the surface. This unique property was utilized to successfully differentiate AgNPs from other silver species, e.g., Ag\(^+\), AgCl and Ag bulk particles. We also found that the ferbam-based SERS method was feasible to detect AgNPs of different surface coatings or sizes. Moreover, SERS signal intensity was positively associated with the concentration of AgNPs, demonstrating the potential of this method to quantify AgNPs. Further, we validated the applicability of this method to detect engineered AgNPs in edible leaves and genuine natural water. The SERS method was also successfully used to monitor the dynamic transformation of AgNPs in dissolved organic matter (DOM)-rich water under different light conditions. This study provides an example of using nanotechnology-based techniques for better monitoring AgNPs and for advancing our understanding of environmental processes and fate of AgNPs.

**COLL 525**

**Silver nanoparticle loaded textile test materials: Impact of particle size and textile type on nanoparticle detection and characterization using multiple techniques**

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Silver nanoparticles (AgNPs) are being employed in an increasing array of commercial products (e.g., textiles and surface coatings) to take advantage of their antimicrobial properties. As a result, it is no surprise that many researchers are conducting studies to assess the environmental, health and safety risks associated with these new products at different stages of their lifecycle (e.g., creation, use, disposal). However, it is important to (A) first assess instrumental capabilities and limitations for nanoparticle detection and characterization using appropriate test materials or controls, and (B) determine a practical and efficient approach for characterizing AgNP containing commercial products. To address these issues, we have developed methods for creating AgNP loaded textile test materials: Specifically, AgNPs loaded onto cotton threads and fabrics via a commonly-used, solution based, technique involving Ag\(^+\) reduction. The loading of AgNPs onto the cotton surface is controllable and directly dependent on the starting concentration of Ag\(^+\). Results demonstrate the effectiveness of loading AgNPs onto cotton threads and fabrics as characterized by an array of microscopy (AFM/SEM) and spectroscopy (XPS, EDS, standard and single particle ICP-MS) based techniques. Additionally, test materials incorporating different particle sizes, as well as synthetic and natural fiber fabrics were examined. We propose, as a direct
result of this investigation, a ‘spectroscopy first’ approach for the efficient detection and characterization of AgNPs in textiles.

COLL 526

**Computationally driven design of bioinspired cells interacting with antimicrobial mimetic nanoparticles**

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Our objective is to design bio-inspired cells composed of different molecular species and investigate their interactions with nanoparticles of various functionalization. Multi-component vesicles are designed to be composed of different representative amphiphilic molecular species present in biological cell membranes [1]. We use a Molecular Dynamics-based mesoscopic simulation technique called Dissipative Particle Dynamics to simultaneously resolve the structural and dynamical properties of stable multi-component vesicles. The model has been used to simulate a particular system regarding peptide-bilayer interactions. We introduce nanoparticles with pin-like geometry which captures the architecture of the α-family of Antimicrobial Peptides (AMPs) which functions as antibacterial agents through membrane perturbation process [2]. These individual molecular species can differ from each other due to the dissimilar chemical properties and molecular geometry of their hydrophilic and hydrophobic groups. We investigate the factors that control the self-organization of the nanoparticles in extracellular aqueous environment and illustrate the dynamics of spontaneous insertion of AMP mimics into bilayer. By tuning the portion of hydrophilic part of the nanoparticle, we are able to model AMPs with different amphilicities and hence to investigate how the length of hydrophilic part regulates the orientation of AMPs in the bilayer. In addition, we explore the effect of the relative concentrations of the molecular species on the stability and properties of the bilayers as well as on the distribution of peptide orientation in the bilayer. The results of our investigations can be used to design artificial peptide and effective cell targeting vehicles with functionalized surfaces for applications in protective coatings for food and agricultural produce.

2. Guangshun Wang, Database-Guided Discovery of Potent Peptides to Combat HIV-1 or Superbugs, Pharmaceuticals 2013, 6(6), 728-758.

COLL 527

**Carvacrol loaded halloysite nanotubes as antibacterial nanoparticles for food-contact materials**
Nanoparticles that are not toxic to humans, but can kill pathogenic microorganisms hold great promise for the prevention and mitigation of foodborne bacterial infections. When incorporated into polymeric matrices, such safe antibacterial nanoparticles can be utilized as antibacterial food packaging materials or as antibacterial coatings for food processing surfaces. Herein we studied the effective loading of halloysite nanotubes with carvacrol molecules and the characterization of antibacterial properties of resulting nanoparticles. Halloysite nanotubes are natural clay nanoparticles with a hollow tubular structure that allow loading and sustained release of active agents. In order to obtain nanoparticles releasing natural and safe antibacterial agents, the empty lumina of halloysite nanotubes were filled with carvacrol molecules that are the active components of the antibacterial thyme oil. The loading efficiency and controlled release of carvacrol from halloysite nanotubes were characterized with Thermogravimetric Analysis and Transmission Electron Microscopy. Carvacrol loaded halloysite nanotubes were shown to stop the growth of food related pathogens such as Pseudomonas putida, Listeria monocytogenes and Aeromonas hydrophila through agar diffusion assays. To investigate the potential of carvacrol loaded halloysite nanotubes as nanofillers in antibacterial nanocomposites for food packaging, they were incorporated into polyurethane and polyethylene matrices. Resulting polymeric films were demonstrated to show antibacterial activity against pathogenic microorganisms. Furthermore chicken samples wrapped with films containing carvacrol loaded halloysite nanotubes presented diminished growth of pathogenic microorganisms as compared to samples wrapped with neat polymeric films. The ability of carvacrol loaded halloysite nanotubes containing polymer nanocomposites to mitigate biofilm formation was also demonstrated as a potential anti-biofilm surface coating material for food processing surfaces.

COLL 528

Rapid size and pH-dependent kinetics of silver nanoparticles in simulated gastric fluid to assess properties of ingested nanoparticles

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Silver nanoparticles (AgNPs) are used in a wide array of commercial products and can enter the human body through oral exposure from food or materials containing them. Thus, it is important to understand the fundamental chemical processes leading to decreases (dissolution) or increases (aggregation) in AgNP size under high salt and...
acidic conditions of the gastrointestinal (GI) tract. In this study, particle growth was observed on the timescale of seconds-to-minutes for solutions replicating the salt content and pH of the human stomach. High time resolution data from Nanoparticle Tracking Analysis (NTA) (30 second) combined with transmission electron microscopy (TEM) were used to explore the kinetics as a function of pH, size, and coating. Greater rates of growth were observed for 20 nm versus 110 nm, with the order of the kinetics changing as a function of pH. Insights into the modification of AgNPs and properties of growth were obtained.

COLL 529

Rhizosphere dissolution of CuO nanoparticles by wheat root exudates in a sand matrix

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Copper oxide nanoparticles (NPs) are used in an expanding range of industries including a potential for agricultural applications as a fertilizer. Accidental spills or misapplication of CuO NPs also may lead to soil contamination. The rhizosphere (rooting zone of plants) has high biogeochemical activity. Plant roots produce a wide range of organic chemicals for bioprotection and enhancing bioavailability of nutrients. Many of these chemicals are metal chelators that may increase the solubility of CuO NPs, thus enlarging the impact of these NPs on plants. This work was directed towards understanding which exudates force increased solubility of CuO NPs and to determine if the level of NP in the growth matrix drives a feedback effect, regarding composition and quantity of exudates.

Wheat seedlings (Triticum aestivum cv Deloris) were grown in a sand matrix for 10 days after 3 days of germination. The sand was amended with 0, 30, 100 and 300 mg Cu/kg dry sand as CuO NPs. Sand was selected as the solid growth matrix as a proxy for soil in terms of plant root morphology, mechanical impedance and water stress, while providing low background dissolved organic carbon for the isolation of root exudates. After plant growth, the pore water was collected from the sand by vacuum filtration, lyophilized and analyzed.

By coupling analytic techniques, including Electro Spray Ionization-Time Of Flight-Mass Spectrometry (ESI-TOF-MS) and Triple Quad MS with geochemical modeling we have identified Cu-ligand complexes that drive the dissolution of CuO NPs; altered biogeochemistry within the rhizosphere also impacted plant uptake of Cu and bioresponse via exudate type, quantity and metal uptake into roots and shoots. This work is relevant to growth of commercially important wheat in the presence of CuO NPs as a fertilizer or as a pollutant.
Nano delivery nutrient strategies to enhance crop nutrition

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Crop production is hamstrung by low nutrient use efficiency caused by nutrient loss to the environment. The Virtual Fertilizer Research Center focuses on identifying improved nutrient packaging and delivery strategies to increase nutrient use efficiency. Nutrient packaging and delivery systems based on nanotechnology have the potential to improve fertilizer use efficiency. The delivery of mineral nutrients in nano form is predicated on a variety of beneficial features, including timing of nutrient release, sustained release of nutrients, synchronization or targeted environmental response, and directed nutrient delivery. Two strategies for nanomaterial delivery into plants can be envisaged. On the one hand, micronutrients from metallic elements can be delivered as nanoparticles (NPs) which can either be taken up directly by the plant or be solubilized in the rhizosphere prior to uptake of the cognate ion. Bulk rock phosphate particles can be prepared as nanoformulations by grinding, or by chemical reactions that produce nanoparticulate P. On the other hand, all mineral nutrients can be encapsulated in nanopolymers that also could either be directly absorbed by the plant, releasing the cognate nutrient in planta, or be engineered to timely dissolve in the rhizosphere, releasing the encapsulated nutrients in sync with the plant’s need. Irrespective of the packaging the nutrients in nanoformulations can be delivered via soil or foliar.

The regulation of nutrient release would benefit the environment in either of two ways, dependent on the agro-ecology. Slow release of fertilizers implies that both leaching and fixation of nutrients could be reduced, permitting a better timing of nutrient availability and plant nutrient needs. This aspect of nano application could be useful in agro-ecologies experiencing the negative consequences of fertilizer overuse. In the case of nutrient-deficient tropical soils, because NPs inherently release soluble ions faster than bulk particles, enhanced and sustained release of nutrients from NPs will be important in supplying nutrients in a quick and timely manner, in contrast to slow release. Despite these potential benefits, nanotechnology in plant fertilization could come with risks for the environment if NPs are misused. Slow release of nutrients from nanoencapsulations could reduce the attainment of biotoxic levels of mineral nutrients, while reducing loss due to leaching or fixation, compared to soluble salt fertilizers.

Monitoring bacterial metabolite production and response to nanoparticles using endogenous fluorescence

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*Pseudomonas chlororaphis* O6 (*PcO6*) is a beneficial root-colonizing bacterium isolated from wheat. It provides drought tolerance and antifungal activity to the host plant. *PcO6* is also a useful surrogate for the human pathogen, *Pseudomonas aeruginosa*. *PcO6* cultures deposited on glass were analyzed with laser scanning confocal microscopy (LSCM) to assess production of secondary metabolites under nanoparticle challenges. The 405 nm laser line of the LSCM was used to excite several endogenous fluorophores having distinct emission windows. The strong intrinsic fluorescence allows for high contrast, label-free imaging where the emission wavelengths and intensities provide additional insight into the metabolic status of the microbe. LSCM operating in the fluorescence spectral mode revealed distinct fluorescence spectra in defined regions of the bacterial films. Upon challenging the microbes with commercial zinc oxide and copper oxide nanoparticles, changes in endogenous fluorescence were observed and correlated to nanoparticle-induced alterations of metabolite production. This was confirmed through use of *PcO6* mutants lacking genes for production of the putative secondary metabolites influenced by these nanoparticles.

**COLL 532**

**Bio-inspired silica nanocapsules through biomolecular engineering**

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Silica nanocapsules have attracted significant interest in recent years due to their core-shell structure, with the core providing high-capacity loading of active components and the shell acting as a protective layer and diffusion barrier enabling the controlled release of actives. However, current approaches are mainly based on templating methods that most often associate with complex processes, including synthesis of core-shell particles using a core material as a template, template removal to make an empty core, and then drug loading after template removal. These methods often require elevated temperatures or extreme pH to remove the core template. Alternatively, we recently developed a novel emulsion and biomimetic dual-templating platform technology for making oil-core silica nanocapsules under mild conditions, including room temperature, neutral pH and without use of any toxic chemicals. The approach is to design bifunctional biomolecules (peptide or proteins) by modularizing a partial sequence encoding surface activity with a series of amino acids having biosilicification ability (Figure 1). Silica nanocapsules are produced by firstly forming nanoemulsions as a result of the surface activity of the bifunctional biomolecules, followed by adding TEOS to initiate biosilicification induced by the catalytic peptide sequence (Figure 1 A). The silica shell can be tuned by controlling the reaction conditions (Figure 1B), and the size of capsules can be controlled by the emulsion droplet size. It has been demonstrated that the slow release of hydrophobic ingredients encapsulated in the oil phase can be
controlled by adjusting the shell thickness of the silica nanocapsules. This technology opens a new facile and environmentally friendly strategy for fabricating capsules that are potentially applicable various fields.

A novel emulsion and biomimetic dual-templating platform technology for making oil-core silica nanocapsules. A. Schematic showing synthesis strategy of the nanocapsules; B. Representative TEM images of silica nanocapsules with different shell thickness.

COLL 533

Novel strategy for ultrasensitive and highly selective detection of infectious pathogens with the help of chemiluminescent labels released from long spacer arm-functionalized magnetic nanoparticles

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When magnetic nanoparticles (MNPs) are applied in bioassay, the detection sensitivity is limited by the inner filter-like effect arising from excess dark MNPs. Herein, we
describe a modified strategy whereby chemiluminescent (CL) labels are released from MNPs in order to eliminate this negative effect. This approach relies on 1) the magnetic capture of target molecules on long spacer arm-functionalized magnetic nanoparticles (LSA-MNPs), 2) the conjugation of streptavidin-alkaline phosphatase (SA-AP) to biotinylated amplicons of target pathogens, 3) the release of CL labels (specifically, AP tags), and 4) the detection of the released labels. CL labels were released from LSA-MNPs through LSA ultrasonication and DNA enzymolysis, the latter proved to be the superior method. In contrast to conventional MNPs, LSA-MNPs exhibited significantly could improve CL detection approach, owing to the introduction of LSA, which was made of water-soluble carboxymethylated β-1,3-glucan (CMG). Detection of hepatitis B virus (HBV) with this technique revealed a low detection limit of 50 fM, high selectivity, and excellent reproducibility. Thus, this new approach may hold great potential for early-stage clinical diagnosis of infectious diseases.

COLL 534

Hybrid platforms for improved bioassay detection limit

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In this work, we present our ongoing efforts for the development of hybrid platforms that can be used to improve the detectability of target analytes. To create the hybrid platforms, the surface of a circular poly(methyl methacrylate) (PMMA) discs and polyethylene terephthalate (PET) were chemically and physically modified with amine functional groups using aminopropyltriethoxysilane and metal nanoparticles. In this regard, thin nanolayers of indium tin oxide and silver were introduced onto the modified surface in two ways: physical method (sputter coated nanofilms; 1 nm, 5 nm, 10 nm) and chemical adsorption method (nanoparticle colloids; low load, medium load and high load). We performed calorimetric sandwich bioassays of glial fibrillary acid protein on these hybrid nanostructures in the presence of a magnetic separator in order to prevent the loss of the analyte complex annexed to the nanolayers. Overall, the bioassay’s calorimetric response and detection limits using hybrid platforms used in conjunction with the magnetic separator compared to the control (magnetic separator with non-hybrid platform) were enhanced approximately 10-fold and 10 pg/mL, respectively.

COLL 535

Enhancing the sensitivity of gold nanoparticle arrays for improved biosensing

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Sarah Unser, Ian Bruzas, Muriel Lemaitre, and Laura B. Sagle
The use of noble metal nanoparticle arrays has been widely applied in areas such as
electronics, catalysis, and optical sensing due to their diverse properties.\textsuperscript{1} Herein, we present the modification and enhancement of the sensitivity of gold nanodisc arrays fabricated through hole-mask colloidal lithography.\textsuperscript{2} The sensitivity was enhanced using three different strategies: growing silver shells around the gold nanodiscs, binding small silver nanoparticles to the gold nanodiscs, and chemically etching the top surface of the gold nanodiscs in the arrays. These modifications change the shape of the gold nanodiscs and consequently produce a localized surface plasmon resonance (LSPR) that is more sensitive to the surrounding media. In addition, increased surface enhanced Raman spectroscopy (SERS) signals were observed upon changing the surface properties of these gold nanodiscs. Data is presented revealing increased LSPR and SERS sensitivity using a UV-Vis spectrometer and micro-Raman setup respectively. Characterization of the modified nanoparticle arrays is carried out using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Using the enhanced LSPR sensing surfaces, drug-protein interactions are monitored through shifts in the plasmon peak due to drug binding bovine serum albumin (BSA).


\textbf{COLL 536}

\textbf{Peptide loaded microgels as antimicrobial surface coatings}

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Implanted biomedical devices and biomaterials are of increasing importance in modern medical care. To decrease the risk of biomaterial-associated adverse reactions we introduce a method to enhance the performance of already used biomaterials.

Surface-bound microgels offer a versatile drug delivery system which decouples triggerability and mechanical properties of the bulk. Easy-to-apply responsive microgels matrices offer both protection and a reservoir for prolonged drug release of biomacromolecules at target site. Biofunctionality of these systems is increased by incorporation of antimicrobial and anti-inflammatory bioactive peptides to selectively target biomaterial-induced complications, not only at a bacterial level but also with host defenses. pH-responsive microgels enables peptide release to be triggered by infection/inflammation related conditions e.g. pH and ionic strength.

Microgels are immobilized through a one-step reaction where carboxylate along the polymer chains of lightly cross-linked poly(ethyl acrylate-co-methacyrylic acid) microgels reacts with introduced epoxy moieties at surface interface. Microgel characteristics such
as, topography and responsiveness to pH and peptide interaction was studied using atomic force microscopy (AFM).

To study peptide loading/release ellipsometry and confocal laser scanning microscopy was used. By varying microgel and peptide characteristics, peptide incorporation and release can be controlled.

We conclude that the microgel coatings keep their intrinsic pH dependent swelling properties in line with previous shown results, although covalently attached. AFM in liquid enables us to follow changes in size of individual microgels and interactions with peptides. Confocal laser scanning microscopy provides a good platform for studying peptide loading and release from microgel coatings in response to media changes.

The versatility of this approach enables us to tune performance of the system and thereby control the release of bioactive peptides, as a complement to conventionally used antibiotics.

References

COLL 537

Water-based polymeric N-halamine biocides

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Water-based polymeric N-halamine precursors, poly(2,2,6,6-tetramethyl-4-piperidyl methacrylate-co-trimethyl-2-methacryloxyethylammonium chloride)(PMPQ), were synthesized by copolymerizing 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPM) with trimethyl-2-methacryloxyethylammonium chloride (TMAC) in different molar ratios
(TMPM:TMAC= 10:90,30:70,50:50,70:30, and 90:10). After chlorine bleach treatment, the TMPM moieties in the new copolymers were transformed into amine-based N-halamines (Cl-PMPQ). The chemical structures of the samples were characterized with \(^1\)H-NMR, FT-IR, and dynamic light scattering. With lower than 70% of the original TMPM content, the resulting CI-PMPQ copolymers were soluble in water, and demonstrated potent antibacterial functions against *Escherichia coli* (Gram-negative bacteria) and *Staphylococcus epidermidis* (Gram-positive bacteria). Furthermore, the new soluble Cl-PMPQ could be coated onto cotton cellulose through a simple padding process at room temperature, and the resulting cellulose demonstrated powerful antibacterial and biofilm-controlling effects.

**COLL 538**

**Controlling the colloidal aggregation of chemotherapeutics**

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Many small molecule drug candidates form colloidal aggregates at micromolar concentrations with diameters ranging from 100-1000 nm\(^1\). Colloid formation is governed by the critical aggregation concentration, below which the compound exists as free drug monomers. Over 20 approved drugs form colloidal aggregates in the 200 nM to 10 µM concentration range\(^1,2\). Colloidal drug aggregates adsorb proteins on their surface, leading to nonspecific enzyme inhibition and false-positives in high-throughput screening. Drug colloids also form in cell culture media, where colloidal formulations of chemotherapeutics reduce activity in cell-based assays\(^3\).

Though colloids have typically been seen as nuisance compounds, their ability to reversibly adopt large particles that on disruption release the monomeric compounds has interesting potential applications. Unfortunately, most aggregates are rarely stable over extended periods; typically the colloids will grow in size by several folds, and over the course of a day will precipitate. Here, we investigate methods for controlling colloidal aggregation and the subsequent impact on colloid stability and interactions with biological systems, as a preliminary effort to see if we can actually exploit colloid formation. Specifically, we use the chemotherapeutic fulvestrant as a model colloid-forming compound to investigate the role of surfactant excipients on colloid formation and stability. We find that surfactants can confer greater size stability to fulvestrant colloids in biologically relevant media with high protein concentrations. Furthermore, the incorporation of fluorophores in colloidal aggregates provides a superior tool for studying their stability in serum-containing media. The results of this work will provide further understanding of how the properties of colloidal drug aggregates impact their fate in biological environments.

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**COLL 539**

*De novo method for uric acid decrystallization using gold nanoparticles and medical microwaves*

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In this study, we demonstrated a rapid method for the decrystallization of uric acid crystals deposited onto a synthetic 3-D platform using gold nanoparticles and an 8 GHz medically approved microwave source equipped with a microwave applicator. A commercial 3-D printer was used to fabricate a polymer platform of acrylonitrile butadiene styrene whereby 3-D structures were built in the shape of actual disjointed bones where gout is likely to develop in humans. With the fabricated 3-D platform, we simulated a gout condition by the formation of uric crystals in the synovial fluid environment. Furthermore, we introduced gold nanoparticles of 20 nm into the gout arrangement and covered the arranged parts with synthetic human skin. Using the microwave generator, the structure (fabricated 3D platform complexed with uric crystals and gold nanoparticles) was subjected to continuous microwaves of powers ranging from 1-20 W. We observed that the amount and the size of the uric acid crystals on a platform with gold nanoparticles were reduced by >80% in a period of 60 seconds using the microwave source at 20 W.

**COLL 540**

*Pharmacokinetic model of a tissue implantable insulin sensor*

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While implantable sensors such as the continuous glucose monitoring system have been widely studied¹, both experimentally and mathematically, relatively little attention has been applied to the potential of insulin sensors. Such sensors could provide feedback control for insulin infusion systems and pumps, and provide platforms for the monitoring of other biomarkers in vivo. In this work, we develop the first
pharmacokinetic model of an affinity sensor for insulin operating subcutaneously in the limit of where mass transfer across biological membranes reaches a steady state\textsuperscript{2}. Using a physiological, compartmental model for glucose, insulin, and glucagon metabolism, the maximum sensor response and its delay time relative to plasma insulin concentration, are calculated based on sensor geometry, placement, and insulin binding parameters for a sensor localized within adipose tissue. A design relation is derived linking sensor dynamics to insulin time lag and placement within human tissue. The model should find utility in understanding dynamic insulin responses and forms the basis of model predictive control algorithms that incorporate sensor dynamics.


COLL 541

Effects of functionalities on drug binding, drug releasing, and biofilm-controlling properties of PMMA based denture biomaterials

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\textit{Candida}-associated denture stomatitis (CADS), caused by colonization and biofilm-formation of \textit{Candida} species on denture surfaces, is a significant clinical concern. We have shown that poly(1-vinyl-2-pyrrolidinone) (PNVP)-grafted denture materials could bind and then slowly release antifungal drugs for months, offering an innovative strategy to control CADS. To provide further information about the structure-property relationships of this new class of CADS-managing denture materials, in the current study, we evaluated the effects of surface functionalities on drug binding and drug releasing behaviors as well as the antifungal activities and biofilm-controlling properties of poly(methyl methacrylate) (PMMA) based denture resins. PMMA denture resins were surface grafted with three kinds of polymers, PNVP, poly(methacrylic acid) (PMAA) and poly(2-hydroxyethyl methacrylate) (PHEMA), through plasma-initiated grafting polymerization. With a grafting yield as low as around 2 wt\%, the three groups of new, functionalized denture materials showed significantly higher drug binding capabilities toward miconazole than the original PMMA denture resin control, leading to sustained drug release and potent biofilm controlling effects against \textit{Candida}. Among these three classes of denture materials, PNVP-grafted resin provided the highest binding capability and the most powerful antifungal and biofilm-controlling activities. These results demonstrated the paramount importance of specific interactions between drug molecules and functional groups on biomaterials in the design of CADS-managing denture materials and other related devices for controlled drug delivery.
Encapsulation of quantum dots in poly (vinylidene chloride) nanocolloids for electronic display coatings

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Herein we describe a technique for encapsulating and protecting non-Cadmium containing Quantum Dots (QD) nanocrystals within a barrier copolymer for use as thin films in LCD backlit displays. Although QDs exhibit the desired properties for electronic applications their photoluminescence are easily destroyed by oxygen and moisture from the atmosphere. And, their processing requires the use of hazardous solvents which is detrimental to the environment. In order to overcome this problem, we have synthesized water-processable Laponite nanoparticle-stabilized colloids with polyvinylidene chloride-based copolymer as the shell and QDs encapsulated within the core of the nanocolloids using a Pickering emulsion approach. Encapsulating the QDs hermetically seals the nanocrystals where oxygen and water vapor transmission rates at standard conditions confirmed that encapsulation protected the QDs from oxygen and moisture (and harmful solvents in the thin films). In so doing, thin films formed with encapsulated QDs exhibited higher photoluminescence with enhanced oxidative stability (or lifetime) compared to their non-encapsulated counterparts. The films formed from these encapsulated QD could potentially be used to enhance the high-definition color gamut of LCD electronic displays.

Multifunctional nanostructures: Fundamentals and applications

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The development of functional nanomaterials with multi-detection modalities opens up new avenues for creating multi-purpose technologies for many applications. Multifunctional nanoparticles take advantage of the physicochemical properties of two or more materials to create a new multifunctional composite nanostructure. The “ideal” nanoparticle would combine multiple detection modalities (magnetic, plasmonic, elastic or inelastic light scattering, fluorescence, storage, tracking, delivery), be stable under biological/industrial conditions, could be easily functionalized, environmentally friendly, and could be prepared in large quantities. Noble metal nanoparticles, particularly gold and silver, have exciting physical and chemical properties that are entirely different from the bulk and meet many of these characteristics. By combining these metallic nanomaterials with either magnetic (Fe2O3) or photocatalytic (TiO2) materials one could create tunable multifunctional nanostructures with multi detection-capabilities, e.g. plasmonic, magnetic, catalytic functionalities. The objective of this talk is to discuss our
recent synthesis and characterization techniques used to create different size, shape, composition and morphology multifunctional nanoparticles and their corresponding applications.

COLL 544

Surfactant ionic liquids with unusually high capacitances for high-temperature flexible supercapacitors

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We report a new class of electrolytes, surfactant ionic liquids (SILs), that give rise to unprecedentedly high intrinsic areal capacitances (~100 to 200 µF/cm²), much larger than the values (~5 to 20 µF/cm²) of other known ionic liquids (ILs) based on smaller anions as well as commonly used aqueous/organic electrolytes. Such high capacitances can probably be attributed to an increased molecular structuring at the nanometer scale due to the presence of large non-polar alkyl chains and charged heads in these fluids. We demonstrate that extremely high gravimetric/volumetric capacitances can be achieved by combining SILs with proper porous electrodes with high surface areas. Due to the extremely wide potential working windows of ILs (~ 4 to 5 V), we show that the SIL-based devices exhibit ultrahigh energy densities. In addition, the SIL-based devices show an increasing capacitance with higher temperatures, which highlights another unique advantage of SILs, which is the suitability for operation at extremely high temperature (~200 °C), with myriad niche applications such as powering sensors and actuators for oil industry downhole operations (above 120 °C), electronics in hybrid electric vehicles (HEV, >60 °C), or military weapons and space equipment. Furthermore, we demonstrate that SILs can be easily polymerized to generate a quasi-solid yet flexible gel-like structure, as well as form seamless binding with current collectors/porous electrodes, for the development of next-generation solid-state highly flexible energy devices.

COLL 545

Aqueous-based fabrication of low-VOC nanostructured block copolymer films as effective marine antifouling coatings

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Nanostructured polymeric films have proven to be effective antifouling coatings due to their diverse chemical, physical, and mechanical properties. Unfortunately, standard fabrication techniques often require extensive annealing procedures that require volatile organic compounds (VOCs) and limit scalability. The following presentation will describe
a novel indirect dissolution technique which results in nanostructured low-VOC block copolymer coatings for marine antifouling applications. The phase transfer of poly (styrene-b-2 vinyl pyridine-b-ethylene oxide) (PS-b-P2VP-b-PEO) triblock copolymer from a water immiscible organic phase to an aqueous phase was studied at various concentrations of poly (styrene-b-ethylene oxide) diblock copolymer phase transfer agent. This resulted in the self-assembly of amphiphilic PS-b-P2VP-b-PEO micelles in an aqueous solution while significantly reducing the release of VOCs. With surface probe microscopy techniques, adhesion forces, topographical images, and mechanical properties of nanostructured PS-b-P2VP-b-PEO films were collected. Adhesion force measurements and zoospore settlement analysis demonstrated the significant ability of nanostructured PS-b-P2PV-b-PEO films to resist protein adsorption.

(A) Schematic representation of water insoluble triblock copolymer transferring from a water immiscible phase to an aqueous phase in the presence of a diblock copolymer phase transfer agent (B) Ratio of triblock copolymer transferred (mT) into the aqueous phase at various concentrations of phase transfer agent.

**COLL 546**

*Polyacrylamide microgels and pore modeled oil recovery performance*

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Crude oil is an internationally important commodity raw material for energy and chemical industries. After primary, by natural pressure, and secondary, by water and gas driven, stages of oil recovery from a well field source, more than two thirds of the original oil remain in the reservoir. In these tertiary reservoirs, the directly water- or even polymer-flooding assisted recovery of reservoir resources are not efficient for displacing resource fluid due to severe heterogeneity of the geologic formations. The displacing agents, e.g., water, prefer low resistance wide pore channel flow of low pressure resistance compared to narrow pore, high pressure resistance flow. Therefore, excess water production becomes a major problem, which leads to early abandonment of otherwise unrecoverable hydrocarbon resources. To solve this problem, polymer gel treatments of the injection wells are being developed to preferentially limit flow through the ‘thief’ zones. Polymer gels can be cost-effective methods to improve sweep efficiency to reduce excess water production during oil recovery.

A novel polyacrylamide microgel was synthesized by a pseudo-inverse emulsion polymerization in the absence of water. Two different crosslinkers were employed in this study to give the particle ‘smart’ properties, e.g., 2 stages of size expansion that are temperature sensitive. When put into water, the original dry particle can swell by as much as 20 times in size under low temperature (e.g., 40 ºC). Exposure to a harsh reservoir environment, for instance, a higher temperature (e.g., 80 ºC), induced cleavage of one of the two crosslinking types to enable further expansion, about 150 times as the original volume. The microgel access to targeted pore channels is thus controlled to realize changes in the reservoir flow profile within the geologic formation.

COLL 547

Effects of clay surfaces on diethyl phthalate degradation in Fenton reactions

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Phthalate esters are a group of widely applied plasticizers to improve durability and flexibility of plastics, which have been detected in surface waters and soils in China. Fenton reactions could be used for their wastewater treatment and soil remediation. Montmorillonite clays are a group of naturally occurred clay minerals, which could greatly adsorb DEP from water solution. There is limited research about effects of clay surfaces on degradation of phthalate esters (dimethyl phthalate, DMP, and diethyl phthalate, DEP) in Fenton reactions. In this study, batch experiments were conducted to investigate effects of clay structures on DEP and DMP degradations either in suspension or on clay surfaces. The results showed that Fe content in montmorillonite clay was important for free radical production. The clay surface would quench •OH radical when Fe content < 3%, and slowed down DEP and DMP degradations in suspension. However, it would produce 20 times more •OH radical in presence of K-NAu-2, in which Fe content was 19.1% and increased the degradation of DMP in
solution and DEP on clay surface. The reaction rate on clay surfaces was increased with adsorbed concentration increasing, and the reaction on K-NAu-2 surfaces was easier than those on the other two montmorillonite clay surfaces. The reaction products of DEP degradation in presence of K-NAu-2 were different from the products in Fenton reactions only. Electron transfer from adsorbed phthalate ester to structured Fe in clay minerals and hydrolysis were hypothesized reaction mechanisms for DEP Fenton degradation in presence of clay minerals. The research would explain the reasons of DEP persistent in water and soil.

**COLL 548**

**Surface-modified Li[Li\textsubscript{0.2}Ni\textsubscript{0.17}Co\textsubscript{0.07}Mn\textsubscript{0.56}]O\textsubscript{2} nanoparticles with AlF\textsubscript{3} as cathode for Li-ion battery**

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Li-rich layered cathode materials have already drawn considerable attention due to their high capacity performance for Li-ion batteries (LIBs). In this work, layered Li[Li\textsubscript{0.2}Ni\textsubscript{0.17}Co\textsubscript{0.07}Mn\textsubscript{0.56}]O\textsubscript{2} (Li-rich) nanoparticles are surface modified with different contents of AlF\textsubscript{3} through facile chemical deposition method. It is found that the AlF\textsubscript{3} surface layers, displaying little impact on material structure, act as buffers to avoid the direct contact of electrode with electrolyte, and thus significantly enhance the electrochemical performances. The 3 wt.% AlF\textsubscript{3}-coated Li-rich electrode exhibits the best cycling capability with much enhanced capacity retention of 83.1% after 50 cycles. Moreover, the rate performance and thermal stability of the 3 wt.% AlF\textsubscript{3} coated electrode are obviously improved as well. Surface analysis indicates that the AlF\textsubscript{3} coated layer can largely suppress the undesirable growth of solid electrolyte interphase (SEI) film, which stabilizes the structure upon cycling.
Since the discovery of self-propelled micro- and nanomotors a decade ago, we have been developing multiple systems in an effort to control the motion at the micro and nanoscale. In contrast to traditional peroxide-powered motors, we developed a more efficient, bubble-free autonomous nanomotor based on a nanobattery. Bimetallic silver-platinum nanorods are powered by self-electrophoresis and show much higher speeds in comparison to similar motors at the same fuel concentrations. This versatile system can also be made into a micropump and will respond to different lighting conditions. We intend to further our understanding of alternate fuels and mechanisms for nanomotors using this and other analogous colloidal systems.
Schematic showing Ag/AgI conversion cycle and how the motion of the silver-based nanorod occurs.

SEM images of (a) pure Ag-Pt nanorods and (b) Ag-Pt nanorods after conversion reaction. (c) Tracking of nanomotors over time after addition of halogen fuel yields an average speed of 7 μm/s and exhibits directed motion.

**COLL 550**

**Spin coating polyelectrolyte coacervate thin films**

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Polyelectrolyte multilayers (PEMUs) are layer-by-layer assemblies of oppositely charged polymer chains used in the production of thin films. The polyelectrolyte chains are bound to one another through entropic driving forces and may be functionalized for a variety of applications. This principle has been applied to the production of
polyelectrolyte complexes (PECs) through solution mixing, which produces an elastic white precipitate. PECs have been dispersed in KBr solution in the form of polyelectrolyte coacervates (PECOVs), which are loosely-bound networks of PEC chains. Coacervates are biphasic mixtures in which one phase is concentrated in a given solute and dilute in the other, where the concentrated phase behaves as an elastic liquid that can be used for spin-coating. Spin-coating coacervates uses little material and short processing times to produce membranes of micrometer thickness with nanometer roughness that can be released from their substrate to yield free-standing films.