COLL 1 Biological recognition-based assembly of peptide nanotubes on surfaces and their functionalizations

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Introduction of biological self-assembly of nanometer-sized building blocks is expected to accomplish the bottom-up fabrications in a more reproducible, efficient, and economic manner. Multiple types of nano-building blocks such as metal/semiconductor nanowires are necessary to be placed at specific locations on surfaces selectively with high precision and reproducibility for more complex nanometer-scale device assemblies. Biological molecular recognitions such as antibody-antigen bindings may be suitable to apply in the building-block assembly since nature always assembles materials with complex functions and structures at room temperature reproducibly. Our approach is to immobilize antibody-coated nanotubes at specific complementary binding positions patterned on surfaces. Because a variety of antibodies and antigens are available, proper choices of antibodies and antigens will enable one to assemble multiple types of nanotubes incorporating different antibodies at the antigen-patterned areas in a single process. We demonstrated to place multiple-types of antibody nanotubes onto their respective complementary binding areas.

COLL 2 Highly active and stable DNAzyme-MWNT hybrids and possible applications

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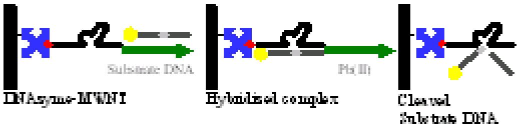
In recent years, the attachment of biological molecules onto carbon nanotubes has received significant interest, especially for applications in biosensing and biorecognition. Most research has been focused on the structure and activity of enzymes on carbon nanotubes. However, DNA may also be designed to be catalytically active with studies primarily focusing on the endonuclease activity of these DNAzymes. We have reported the generation and characterization of DNAzyme-carbon nanotube conjugates by attaching biotinylated DNAzyme to streptavidin-functionalized MWNTs. The resultant DNAzyme-MWNT conjugates exhibited Michaelis-Menten kinetics and multiple catalytic turnovers. The specific activity of the nanoscale conjugates was ca. one-third of that for free soluble DNAzyme. The DNAzyme-MWNT conjugates might provide unique opportunities as templates for nanoscale assembly and as nanoscale cellular therapeutics that rely on the RNA cleaving ability of DNAzymes.



COLL 3 Controlling the cellular response of nanomaterials

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The in vitro biological effects of water-soluble nanomaterials are examined in an effort to evaluate the fundamental mechanisms that contribute to the cytotoxicity of classic engineered nanoparticles. Here we used a water-soluble fullerene species, nano-C60, a fullerene aggregate that readily forms when pristine C60 is added to water. Nano-C60 was cytotoxic to human dermal fibroblasts (HDF), human liver carcinoma cells (HepG2), and neuronal human astrocytes (NHA) at doses > 50 ppb (LC50=2-50 ppb, depending on cell type) after 48 hour exposure. Nano-C60 disrupts normal cellular function through lipid peroxidation. The integrity of cellular membrane was examined by monitored

the peroxy-radicals on the lipid bilayer. Subsequently, glutathione production was measured to assess the cell's reaction to membrane oxidation. The damage to cell membranes is observed both with chemical assays, and confirmed physically by visualizing membrane permeability with high molecular weight dyes. With the addition of an antioxidant, L-ascorbic acid, the oxidative damage and resultant toxicity of nano-C60 was completely prevented.

COLL 4 Microgel bioconjugates for mediation of cellular interactions

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The synthesis of core/shell poly(N-isopropylacrylamide) (pNIPAm) and poly(N-isopropylmethacrylamide) (pNIPMAm) hydrogel nanoparticles with radius of gyration near 50nm is described. The particle size and volume transition were measured by dynamic light scattering and multi-angle laser light scattering. To enable in vitro studies of cellular uptake, the particles contain 4-acrylamidofluorescein (AFA) in the core as a fluorescent marker and N(3-aminopropyl)methacrylamide (APMA) in the shell, to allow folic acid coupling to the microgels. The folic acid is then used to target the particles to tumor cells, which overexpress the folate receptor. Additionally, PEG-based cross-linkers were explored in order to render the nanogels resistant to non-specific adsorption. These particles will be discussed with respect to their physico-chemical properties in the context of biological studies.

COLL 5 New sensing surface based on codeposition of multiwalled nanotubes and sol-gel silicon dioxide

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Dispersing carbon nanotubes into tetramethyloxysilane can result in a stable colloidal sol that can be subsequently cast onto the conducting substrate surfaces. This resultant sol-gel- carbon nanotube network can incorporate electroactive species such as ferricyanides. By using multiwalled carbon nanotubers (MWCNTs), this composite has showed excellent electrocatalytic behavior that has potential for voltammetric measurement of trace environmental contaminants such nitrite, chromium (VI) and biosensing towards glucose.

Various chemical and electrochemical means have been used to characterize the resultant composites. While exact micro morphology is not well understood at this stage, it appears the networked silicon dioxide with cavities filled with MWCNTs that also possess high surface over volume ration which are specially accessible to redoxactive small molecules as well as macro biomolecules such as enzymes. These new functional composites shed promise for fabrication of new sensing devices.

This work was supported by Starter Award from SACP (Pittsburgh, PA)

COLL 6 Bioengineered flagella nanotube composites of mesophilic bacteria

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Protein nanotubes present unique opportunities for the generation of novel composites with inorganic and organic components and the fabrication of nanoscale devices for applications as sensors,

separation media, and templates for the generation other nanotube structures. Our research program is focused on engineering flagellin (FliC) proteins and their flagella by site directed mutagenesis in which specific binding groups such as peptide loops have been introduced in the D3 domain. We have engineered FliC proteins of mesophilic bacteria with a thioredoxin loop in the D3 domain which has been further modified with various peptide loops such as histidine and cysteine loops. Various nanoparticles such as Au, Ag, and Cd have been bound to the histidine loops to obtain ordered arrays of nanoparticles on flagella nanotubes. Cu and silica nanotubes have been generated by the reduction of bound Cu2+ ions and the acid hydrolysis of silicate ions. Flagella with cysteine loops self-assemble through the formation of disulphide bonds to yield flagella bundles. These can be dissociated by breaking the disulphide bond by the addition of reducing agents such as TCEP. These bundles can be visualized with a fluorescence microscope by staining with nanoorange. The cysteine loops flagella and their bundles exhibit interesting CD and near infrared spectra which indicate their three dimensional structures. Salient results from these studies will be presented.

COLL 7 SGlutathione-capped CdTe quantum dots: synthesis and applications in cell imaging

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Glutathione-capped CdTe quantum dots (QDs) have been synthesized in aqueous solution and the fluorescence emission is tunable between 500 nm and 650 nm. The as-prepared QDs have a quantum yield (QY) of 30% to 45%, and the bandwidths of the fluorescence peaks is as narrow as 30 nm, comparable with most organometallically synthesized QDs. Purified glutathione-capped CdTe QDs were monodispersed with a particle size of less than 5 nm. These QDs were highly soluble and stable in a wide pH range and in biological systems. To demonstrate their potential for cell imaging, the glutathione-capped CdTe QDs have been conjugated with biotin, and immunostaining and fluorescence imaging were conducted with the biotin-labeled QDs.

COLL 8 Gd(III)-functionalized fluorescent quantum dots for multimodal imaging probes

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The incorporation of magnetic property onto the same fluorescent nanoparticle probes is highly desirable for in vivo biolabeling applications because they can be detectable in multiple modes (both optical and magnetic imaging). Multimodal probes of Gd^{III}-functionalized, silica-coated CdS:Mn/ZnS quantum dots that exhibit yellow fluorescence and strong paramagnetism are reported. Successful attachment of Gd^{III} ions to fluorescent silica-coated quantum dots and their magnetic resonance imaging (MRI) properties will be demonstrated. Quantum dots with an inner crystal diameter of ~3 nm and a 4-7 nm thick silica layer were synthesized and demonstrated to exhibit good MRI contrast in both longitudinal (T_1) and transverse (T_2) proton relaxation time-weighted images. An average number of Gd^{III} ions per quantum dot of ~107 results in this good contrast. Fast T_1 and T_2 relaxivities of 20.5 and 151 $mM^{-1}s^{-1}$ have been attained, respectively. The use of these functionalized quantum dots for in vivo imaging using a rat model will be discussed.

COLL 9 Utilizing the electronic industry's tricks for transistor fabrication for development of new delivery colloidal vehicles for nanomedicine applications

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The delivery of therapeutic, detection and imaging agents for the diagnosis and treatment of cancer patients has improved dramatically over the years with the development of nano-carriers such as liposomes, micelles, dendrimers, biomolecules, polymer particles, and colloidal precipitates. While many of these carriers have been used with great success in vitro and in vivo, each suffers from serious drawbacks with regard to stability, flexibility, or functionality. To date, there has been no general particle fabrication method available that afforded rigorous control over particle size, shape, composition, cargo and chemical structure. By utilizing the method we has designed referred to as Particle Replication In Non-wetting Templates, or PRINT, we can fabricate monodisperse colloidal particles with simultaneous control over structure (i.e. shape, size, composition) and function (i.e. cargo, surface structure). Unlike other particle fabrication techniques, PRINT is delicate and general enough to be compatible with a variety of important next-generation cancer therapeutic, detection and imaging agents, including various cargos (e.g. DNA, proteins (fluorescently-labeled avidin (MW 68 kDa)), chemotherapy drugs (doxorubicin), biosensor dyes, radio-markers, contrast agents), targeting ligands (e.g. antibodies, cell targeting peptides) and functional matrix materials (e.g. bioabsorbable polymers or stimuli responsive matrices). PRINT makes this possible by utilizing low-surface energy, chemically resistant fluoropolymers as molding materials and patterned substrates to produce functional, harvestable, monodisperse polymeric particles. PRINT has several distinct advantages over other vector fabrication techniques in that the colloidal particles are monodisperse and shape specific. In addition, no surfactants condensation agents, etc. are required.

COLL 10 Bacteriophage-nanocrystal conjugates: Probing local protein structure in vitro using surface enhanced Raman spectroscopy

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In this paper, we report on the use of surface enhanced Raman spectroscopy (SERS) to rapidly acquire vibrational spectra of intact bacteriophages in solution. Our strategy is to covalently attach structurally well-defined Au and Ag nanocrystals (NCs) to the surface of bacteriophages. Using this approach, it is no longer necessary to attach bacteriophages to the surface of a metal, allowing information to be obtained in vitro. In addition, due to the strong distance dependence of surface enhancement, SERS spectra report on local protein structure. Experimental tactics for conjugating NC to bacteriophage coat proteins will be discussed, and preliminary SERS and Raman optical activity data will be presented. Finally, bacteriophage-NC conjugates have important applications in biosensing, such as in the detection of pathogenic cells, and these applications also will be discussed.

COLL 11 Characterization of surface-bound DNA strands by nonlinear optics

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Second harmonic generation (SHG) was used to study DNA strands at the silica/water interface as a function of salt concentration. SHG takes advantage of the intrinsic negative charges on the phosphate groups along the DNA backbone, eliminating the need to use labels. A thermodynamic analysis of the functionalized DNA interfaces was performed to determine the interfacial charge density, the interfacial potential, and the change in interfacial energy density. The melting profile of the tethered oligonucleotides with their complementary sequence and the chirality of the DNA double helix as a result of changes in salt concentration was investigated. Sum frequency generation was

used to further characterize the oligonucleotide surfaces by measuring their vibrational spectra. The information elucidated from the study of the interactions between surface-bound DNA and biological target molecules is relevant to the field of biodiagnostics and can be used to improve and optimize biosensor design and development.

COLL 12 Effect of ɑ-lactalbumin on lipid / oil / water mixtures using SAXS

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Recently we have found that the globular protein ɑ-lactalbumin can alter the phase behavior of an anionic surfactant, AOT, in equal volumes of oil and water. We studied the effect on phase structures using SAXS, which shows that the addition of ɑ-lactalbumin increases the size of w/o microemulsion droplets, and promotes the formation of various aqueous nanostructures. We compared these results with effects of ɑ-lactalbumin on the phase behavior of phospholipids. In systems with the zwitterionic phosphatidylcholine alone, there was only a weak interaction between the protein and surfactant. However, we found that in the presence of a negatively charged fatty acid, ɑ-lactalbumin increases the size of the w/o microemulsion droplets. We explain such influences of the protein in terms of the change in the spontaneous curvature of the surfactant interface. This study allows us to have a broader understanding of the influence of protein on surfactant self-assembly.

COLL 13 Label-free diagnostics of single base-mismatch DNA hybridization on gold nano-particles using hyper-Rayleigh Scattering technique

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We present for the first time the HRS assay for ss-DNA sequence recognition based on the difference in electrostatic properties between ss-DNA and ds-DNA. Here we demonstrated that the hyper–Rayleigh scattering (HRS) technique could be used for ultra-sensitive detection of single base-pair mismatch oligonucleotide strands on gold nanoparticle without any tagging. The mechanism of HRS signal enhancement after hybridization have been discussed.. A key advantage of the HRS technique is that one can avoid tagging of any dyes to probe protein and DNA in solution and it can be 1-2 orders of magnitude more sensitive than the usual colorimetric technique

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COLL 14 Zirconium-phosphonate surfaces for oligonucleotide arrays: An XPS investigation of probe binding

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Zirconium-phosphonate surfaces have been shown to bind 5'-phosphate modified oligonucleotides, which led to the development of oligonucleotide microarrays based on this system. The zirconium-phosphonate surface selectively binds 5'-phosphate modified oligonucleotides over unmodified oligonucleotides. A question which still needs to be answered is the surface coverage of the probe molecules. To determine this, 5'-phosphate modified oligonucleotides immobilized on a zirconium-phosphonate surface were studied with X-ray photoelectron spectroscopy (XPS). Using the N1s peak and the homogeneous overlayer-substrate model the surface density of oligonucleotide could be calculated. Several methods, including variable-angle XPS, were employed to correct for surface contamination on the bare zirconium-phosphonate surface. It had been seen in hybridization experiments that probes with an 11G spacer, compared to probes containing no spacer, increased target capture. To determine whether this was due to improved probe immobilization or hybridization efficiency, XPS was used to study probes containing G11, A11, and T11 spacers. This showed that the G11 spacer enhanced probe binding.

COLL 15 Shear alignment of non-ionic wormlike micelles observed by rheo-NMR

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Orientational order produces myriad nonlinear effects in complex fluids such as polymer micelle solutions, liquid crystals, and anisotropic colloids. Wormlike micelles (WLMs) exhibit especially fascinating rheological properties since the component molecules order relative to the tube axis, which itself may act as a supramolecular polymer backbone. Equilibria between wormlike and spherical micelles may be controlled using temperature, concentration, or additives to vary properties (e. g., viscosity) over several orders of magnitude. We have investigated a new class of WLMs composed of non-ionic triblock copolymers (PEO-PPO-PEO) mixed with alcohol additives to stabilize the core. We have employed in situ rheo-NMR spectroscopy and microscopy in a couette shear cell to observe the first shear-induced alignment and banding in a non-ionic block-copolymer system. Deuterium-labeled additives show spectral splittings, assessing the molecular alignment versus shear rate. Proton NMR microscopy probes shear banding across the couette cell gap with resolutions down to 20 microns.

COLL 16 Mechanism of gel formation of metallo-supramolecular polymers

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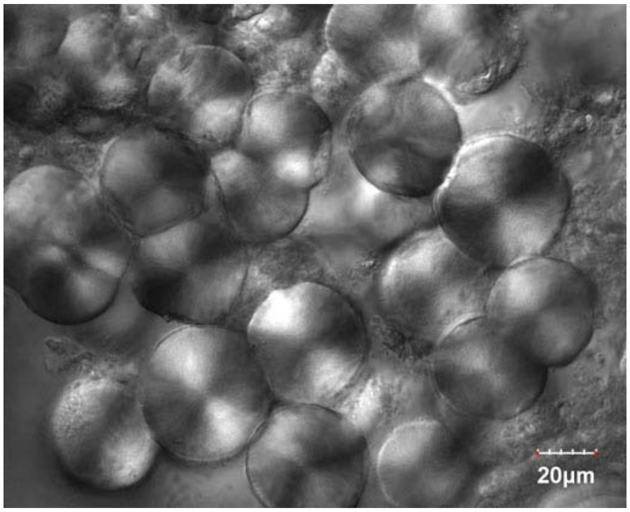
Utilizing metal-ligand binding as the driving force for the self-assembly of a ditopic ligand, which consists of a 2,6-bis-(benzimidazolyl)-4-hydroxypyridine unit attached to either end of a penta(ethylene glycol) core, three series of metallo-supramolecular gels have been prepared in the presence of a transition metal ion (Zn(II)) and with varying amounts of a lanthanoid metal ion (La(III)) having different binding capabilities. The resulting materials exhibit dramatic reversible responses to a variety of stimuli, including thermal, mechanical, light and chemical. Microscopy examinations reveal that the supramolecular metal-ligand coordination species form globular colloidal particles in acetonitrile solvent. Overall interactions among these swollen microgel colloidal particles result in a flocculated gel structure. Rheological studies show that these gels are strong solids with pronounced non-linear viscoelasticity, which is due to the particular colloidal structure and the nature of supramolecular interactions between ligand monomer and metal ions.



COLL 17 Synthesis and assembly of nematic organogels and nanocomposites

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Dispersions of hydrophobically-modified clay particles can form nematic gels in organic liquids such as toluene and xylene. The dispersions are viscous sols at low particle concentrations and transparent gels at high concentrations (~ 10 wt.%). When examined under polarized light, the gels show a strong static birefringence, which is reminiscent of nematic liquid crystals. We have characterized these dispersions by combining visual observations, optical microscopy, dynamic rheological techniques, X-ray diffraction and small-angle neutron scattering. Additionally, we are using these nematic organogels as a route towards the in-situ synthesis of nematic polymer nanocomposites. The characterization of the nanocomposites using TEM and AFM will also be discussed.

COLL 18 Structure development in nanocomposite multilayered films made from solution

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We investigate the structure development in multilayered PEO/Montmorillonite and PEO/Laponite nanocomposite films made from solution. In solution the clay particles are exfoliated and act as multifunctional cross-links to the polymer building a network. The shear orientation of this network combined with the simultaneous solvent evaporation leads to hierarchical multilayer formation. The resulting films have highly ordered structures on all length scales.

COLL 19 Analytical ultracentrifuge study of micellization of surfactant mixtures

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Nature of supramolecular aggregates formed by mixed surfactants has a marked effect on their adsorption on particles and their resultant interfacial behavior. In order to derive relationships between aggregation behavior and the structure of surfactants, it is necessary to acquire quantitative information on the type of micellar species present in the system. In this study, information on size and shape of micelles is obtained for two combinations (nonionic/anionic and nonionic/cationic) of surfactant mixtures by analytical ultracentrifugation technique. While only one peak indicative of one type of micellar species was identified in mixed dodecyl maltoside(DM) and sodium dodecyl sulfate(SDS) system, at a low concentration of 10mM with the sedimentation coefficient shifting from 1.4 S to 3.6 S with increase of DM ratio, two peaks were found at high concentrations (>50mM). In the case of DM/DTAC mixtures, two micellar species were found at a concentration of 5mM with sedimentation coefficients 4.2 S and 7.4 S, which are greater than 3.6 value for DM alone, suggesting growth of micelles and coexistence of different micelles resulting from the strong intermolecular interactions. In contrast to the above, interestingly, DM/Gemini 12-4-12 shows the presence of only one type of micelle. These differences are attributed to the variations in molecular packing resulting from differences in molecular geometry as well as electrostatic repulsion between head groups of the ionic components. This suggests a means to obtain desired assemblies by designing appropriate combinations of surfactant structures.

COLL 20 Microemulsions formed with novel fluorinated surfactants in supercritical carbon dioxide

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A series of novel fluorinated analogues of AOT surfactants, the sodium salt of bis- (3,3,4,4,5,5,6,6,6-nanafluoro-1-hexanol) sulfosuccinate (CF3(CF2)3CH2CH2OOCCH2-CH(SO3Na)COOCH2CH2(CF2)3CF3, di-HCF5), the sodium salt of bis(2,2,3,3-tetra- fluoro-1-propanol) sulfosuccinate (HCF2CF2CH2OOCCH2CH(SO3Na)COOCH2CF2- CF2H, di-HCF2), the sodium salt of bis(2,2,3,3,3-pentafluoro-1-propanol) sulfosuccinate (CF3CF2CH2OOCCH2CH(SO3Na)COOCH2CF2CF3, di-CF2), the sodium salt of bis(2,2,3,4,4,4-hexafluoro-1-butanol) sulfosuccinate (CF3CFHCF2CH2OOCCH2CH- (SO3Na)COOCH2CF2CFHCF3, di-HCF3), were synthesized and characterized by 1H NMR spectroscopy and elemental analysis. The pressure-temperature phase behavior for water-in-CO2 microemulsions stabilized by the four surfactants was tested and the P-T diagrams were determined. In the phase behavior experiments, the pressure up to 35 MPa, the temperature up to 65 0C and the water-to-surfactant molar ratio (W0) from 10 to 30 were tested. The phase behavior of these surfactants in water-in-CO2 microemulisons was affected by temperature, pressure, W0, and variety of surfactants. The cloud-point pressure in microemulsion stabilized by the four fluorinated analogues of AOT surfactants increased with increasing temperature. At a fixed temperature, the cloud-point pressure increased with increasing of W0. However, the cloud-point pressure was slightly affected by the increasing of surfactant concentration at a settled W0. The phase behavior for water-in-CO2 microemulsions at different Cd(NO3)2 and Na2S concentrations in the aqueous phase with the surfactant of di-HCF5 was also determined, which is useful for the formation of CdS nanoparticles in our further studies.

COLL 21 Fluorescence properties of an anisotropic structure formed by cyclodextrin inclusion complex

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Cyclodextrins (CDs) are cyclic oligosaccharides, and have been studied extensively as a host molecule with numerous organic molecules. Among them, gamma-cyclodextrin (g-CD), consisting of eight glucose units, has a large cavity with diameters of 9.5 Å, and this large cavity size allows the inclusion of molecules and the proximity of the molecules can lead to electronic interaction among them. In this presentation, we describe unusual anisotropic behavior observed in the complex of linear acetylene dye with g-CD. When mixed with g-CD in high enough concentrations, the dye forms an anisotropic liquid, as observed using a polarized light microscope. We have used various fluorescence measurements in order to investigate the nature of the complex formed in aqueous solution, including fluorescence anisotropy. The experimental results reveal that the appearance of anisotropy depends on the concentrations of both molecules and that the rotational diffusion behavior is much affected within CD cavity.

COLL 22 Molecular surface nanostructures and nanosheets by e-beam lithography of self-assembled monolayers

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Molecular self-assembly requires molecular resolution surface templates. To fabricate high-resolution (<10 nm) surface templates, we modify surface bound self-assembled monolayers (SAMs) by e-beam lithography. In functionalized aromatic SAMs, the electrons cross-link the aromatic cores and chemically convert the terminal groups, for example from nitro to amino. Hence, e-beam lithography creates localized surface groups to which other molecules may couple. These molecular patterns can be transferred into metals and semiconductors, and can be utilized for a laterally controlled electrochemical deposition. Molecular surface nanostructures have also been used to immobilize other molecular entities, such as dyes, polymers, and biomolecules. Molecular surface nanostructres can also be removed from the substrate and nanosheets, i.e. free-standing membranes with the thickness of a single molecule, are obtained.

COLL 23 Sub-10nm patterns defined by electron beam lithography and molecular liftoff

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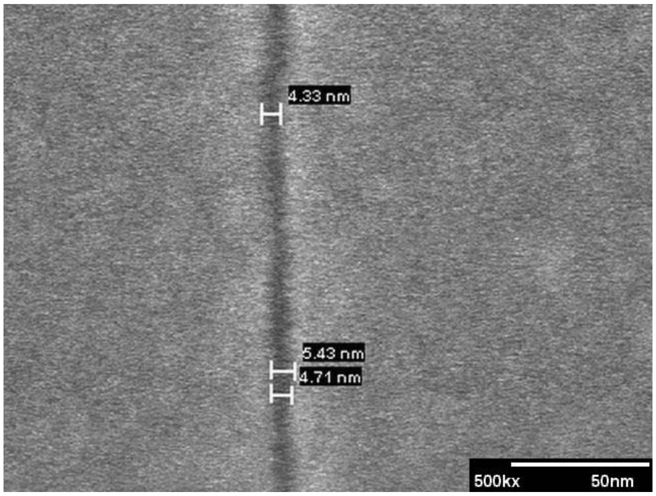
Electron beam lithography (EBL) is a powerful tool for sub-10-nm scale patterning. However, patterning at this scale requires several modifications to normal processing methods. We have demonstrated sub-30 nm resolution patterning of nanoparticles, self-assembled monolayers and biomolecules using a clean liftoff-like process. We demonstrate here 5 nm trenches in PMMA on silicon substrate defined by EBL using an Elionix-7700 system. At this trench width, transport of molecules to the trench bottoms becomes difficult unless ultra-thin (sub 40nm) resists are used. Ultrasmooth substrates must be used and care is required to obtain clean development down to the trench bottoms and to minimize the amount of PMMA debris after liftoff. The combination of ultra-high resolution EBL and molecular liftoff can be used to fabricate protein nanostructures and to pattern various kinds of molecules and particles on the scale of a few nanometers.



COLL 24 Applications of scanned probe lithography for chemical assembly

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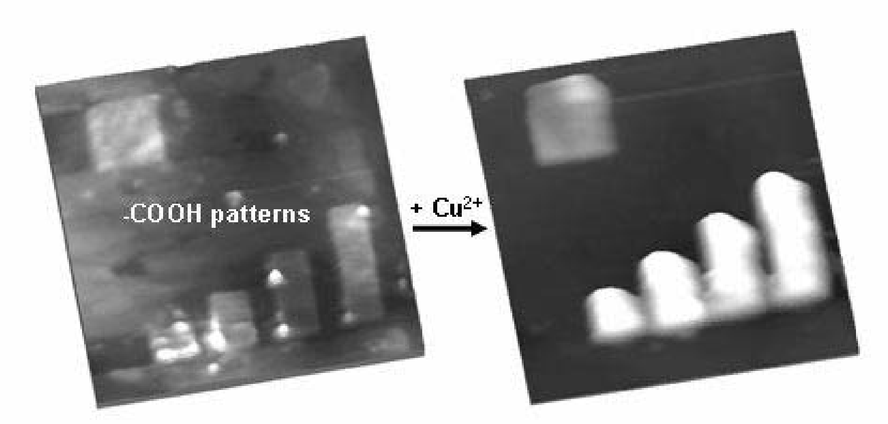
Scanned probe lithography (SPL) offers the capability for patterning surface features with nanoscopic dimensions. Moreover, the ability of SPL to generate structures of variable sizes in solution conditions allows for a range of complex architectures to be constructed by combining nanopatterning with chemical self-assembly techniques. Here we report on the application of SPL for the fabrication of nanoscopic metallic features on metal and semiconducting substrates using a combination of SPL and electroless metal and nanoparticle deposition. Using these approaches, confined metal-molecule-substrate junctions can be created for use in the design of nanoscale optoelectronic devices. Details for controlling the writing parameters for optimizing feature formation will also be described.



COLL 25 Atomic resolution patterning of organosilicon heteromolecular nanostructures using feedback controlled lithography

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Ultra-high vacuum scanning tunneling microscopy is employed for the nanofabrication of atomically registered heteromolecular organosilicon nanostructures at room temperature. In particular, feedback controlled lithography (FCL) is used to remove individual hydrogen atoms from the chemically inert Si(100)-2x1:H surface. The resulting dangling bonds selectively react with organic molecules, thus enabling the formation of organosilicon nanostructures. For example, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) is compatible with single molecule patterning as it quenches individual dangling bonds to form silicon-oxygen covalent bonds. On the other hand, styrene undergoes self-directed one-dimensional growth from FCL patterns following a mechanism analogous to free radical polymerization. Using multi-step FCL, the TEMPO and styrene chemistries can be combined to realize heteromolecular organosilicon nanostructures. In addition, organohalide molecules, such as 4-bromostyrene, provide further opportunities for tailoring the chemical reactivity of silicon. Ultimately, this approach can be used for fundamental studies and fabricating prototype devices that require atomically registered organic molecules on silicon.

COLL 26 High resolution patterning in organo-mercaptan self-assembled monolayers using electrostatic nanolithography

Sergei F. Lyuksyutov[1], Pavel B. Paramonov[2], Olga V Mayevska[2], Richard Vaia[3], Shane Juhl[3], Kazuo Umemura[4], Hiroaki Tobari[4], and Masahiko Hara[5]. (1) Departments of Physics, Chemistry and Polymer Engineering, The University of Akron, Akron, OH 44325, Fax: 330-972-6918, sfl@physics.uakron.edu, (2) Departments of Physics and Polymer Engineering, The University of Akron, (3) Materials and Manufacturing Directorate, Air Force Research Laboratory, (4) Musashi Institute of Technology, Tokyo 158-8557 Japan, (5) Local Spatio-Temporal Functions Laboratory, Frontier Research System, RIKEN

A concept for robust lithographical nanopatterning in alkylthiolates assembled on Au(111) based on electrostatic interactions between atomic force microscope tip and the monolayer has been suggested. The formation of the multi-layered nanostructures (1-9 nm height) occurs through the conformational rearrangement of oranomercaptan moieties. A weakly (-9-15 V) biased tip induces spatially controlled desorption of the molecules, localized to the nanoscale region on the surface, followed by the reorganization of the desorbed species and the stabilization of the nanostructure by intermolecular interactions. The bonding between the desorbed sulfur ends of alkylthiolates enhances the nanostructure stability. The demonstrated concept provides an additional spatial dimension for nanoscale architecture in SAM. Selection of the patterning conditions (primarily – humidity of the ambient air) and of the functionalization of alkyl chains would provide enhanced control over the multilayer structure formation.

COLL 27 Massively parallel Dip-Pen Nanolithography

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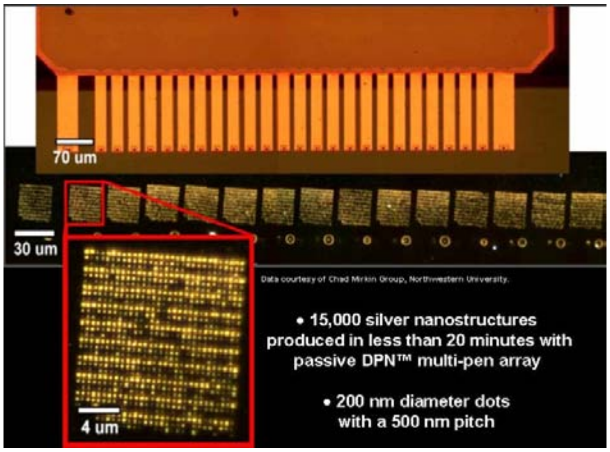
Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolution matching that of e-beam lithography, and allows one to generate nanoscale arrays of a variety of materials ranging from oligonucleotides to proteins to conjugated polymers. This talk will describe how the capabilities of DPN can bring together the divergent fields of top-down lithography and bottom-up self-assembly to study fundamental surface science phenomena, biological (cell, virus, protein, DNA) recognition, and nanoscale electronics. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

COLL 28 Dip-Pen Nanolithography: Ultimate tool for biodiagnostics and advanced electronics

Nabil A. Amro[1], Khalid Salaita[2], Sergey Rozhok[3], Sandeep Disawal[1], Roger Shile[1], Joseph S. Fragala[1], and Chad A. Mirkin[2]. (1) NanoInk, Inc, 1335 W. Randolph Street, Chicago, IL 60607, Fax: 312-525-2972, namro@nanoink.net, (2) Department of Chemistry and Institute of Nanotechnology, Northwestern University, (3) Department of Chemistry and International Institute of Nanotechnology, Northwestern University

The ability to control chemistry of surfaces on the 1-100 nm length scale is a fundamental and exciting challenge in nanoscience and nanotechnology because it opens new possibilities in fields ranging from basic surface science to biomedicine. Dip Pen Nanolithography (DPNT) is a scanning probe-based lithography technique in which an atomic force microscope tip is used to deliver chemical reagents (from small organic molecules to biological polymers, and from colloidal particles to metals ions) directly to nanoscopic regions of a target substrate (from metals to insulators and modified-surfaces). The combination of resolution, registration, and direct-write capability offered by DPNT distinguish it from any alternative lithographic strategy and make DPNT a promising tool for patterning a variety of nanostructures. In this talk we describe DPNT methods and tools for patterning both inorganic and biological materials using multi-probe technology for parallel writing (25,000 pens), and discuss DPNT applications in areas such as biological diagnostics and fundamental nanoscale science. Examples of single virus particle control will be presented.



Data courtesy of Chad Mirkin Group, Northwestern University.

- 15,000 silver nanostructures produced in less than 20 minutes with passive DPN™ multi-pen array
- 200 nm diameter dots with a 500 nm pitch

COLL 29 Manipulation of particle adhesion and motion using distributed surface features

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While there is much to be gained in the development of smart materials from the use of regular patterns and immobilization of specialized biomolecules, entirely new classes of dynamically responsive materials will result from the incorporation of controlled distributions of surface functional groups and nanometer-scale regions of controlled surface chemistry. For instance, we find the ability to tune the adhesion / capture rates of particles on a collector using randomly distributed 10-nm scale adhesive patches, and report selective behavior for the curvature of the objects impinging on the collectors. We also observe the ability to control the type of interfacial motion, from relatively quick binding to extended rolling. We attribute these behaviors to the spatial distribution of adhesive moieties in addition to the local adhesion strength. In addition to experimental results, this talk presents modeling that sets out design rules for surfaces with targeted dynamic behavior.

COLL 30 Direct measurement of adhesion between identical polyelectrolyte brush layers in the presence of trivalent counterions

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Polyelectrolyte brushes in the presence of trivalent counterions (Al3+) exhibit significantly different behavior than with monovalent counterions. When trivalent counterions are present in small amounts, the brush shrinks from the highly stretched structure characteristic of low amounts of monovalent salt. Strong attraction also appears when the two brushes were separated in the presence low amounts of trivalent salt. The behavior of the brush is dominated by this attractive interaction between the polyelectrolyte segments, which is electrostatic in nature and can be screened by increasing the ionic strength. In order to develop the adhesion, the two brushes have to be brought into contact. The magnitude of adhesion scales with the compression ratio to the -0.69 power, in agreement with theoretical prediction. This is in agreement with the hypothesis that the inter-layer attraction between the two brushes results from the condensed counterions in the interpenetration zone.

COLL 31 Watching colloids rotate in crowded environments

Steve Granick, Liang Hong, Stephen Anthony, and Liangfang Zhang, Materials Science, Chemistry, and Physics, University of Illinois, 1304 West Green St., Urbana, IL 61801, sgranick@uiuc.edu

Particle tracking methods have been used to follow the rotation of Janus particles whose fluorescence optical emission was optically modulated to reveal rotation of the particle. From statistical analysis of single-particle trajectories, not only the translational but also the rotational diffusion coefficients are deduced. A surprising contrast between these two diffusion coefficients is found, which is quite different from that characteristic of molecular glasses. Experiments are underway in which the Janus particles with chemical asymmetry are linked into dimers, trimers, and so forth. This in turn has provocative consequences for the observed translation and rotation.

COLL 32 Interactions between surfaces bearing charge patch mosaics

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Surfaces bearing mixed charge domains are ubiquitous in areas ranging from cell and protein surfaces to colloidal dispersions. Using a surface force balance we have measured directly the forces between two surfaces bearing a mosaic of mixed charges across water and across aqueous salt solutions. Our results show remarkable long-range interactions, whose range and magnitude appear

to depend on the dimensions of the charged domains themselves or on the electrostatic screening length, whichever is the smaller. We attribute these forces to charge correlations between the surfaces.

COLL 33 Surfactant interactions with polyelectrolytes: Microscopic binding and macroscopic gel particles

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Mixing of oppositely charged surfactants and polyelectrolytes in aqueous solutions can lead to associative phase separation, where the concentrated phase assumes the form of a viscous liquid, gel, or precipitate. This phenomenon can lead to the formation of gel-like particles whose size and polydispersity can be controlled. Specifically we present phase behavior and structural studies of gel-like particles formed by mixing drops of N,N,N-trimethylammonium derivatized hydroxyethyl cellulose (JR-400) polyelectrolyte solution with oppositely charged anionic and catanionic surfactant solutions. The resulting gel particles range in diameter from approximately 200 to 4000 microns. The structure of the particles is governed by the solution composition and the method of preparation, while the particle stability is governed by phase behavior alone.

COLL 34 Development of interpenetrating hydrogel networks for applications in ophthamology

Curtis W. Frank[1], David J. Myung[1], Won-Gun Koh[1], Jungmin Ko[1], Nabeel Farooqui[1], Michael R. Carrasco[2], Christopher Ta[1], and Jaan Noolandi[1]. (1) Chemical Engineering, Stanford University, 381 North-South Mall, Stanford, CA 94305, Fax: 650-723-9780, curt.frank@stanford.edu, (2) Santa Clara University

Fully interpenetrating hydrogel networks prepared from poly(ethylene glycol) as the first network and poly(acrylic acid) as the second are being studied as candidate materials for applications in ophthamology. Control of molecular weight between crosslinks and pH of the swelling solution leads to systems with ultimate tensile strengths up to 85 times greater than the individual networks, water content of 75%, glucose permeability comparable to the human cornea, and optical clarity. The hydrogels have been modified with a surface coupling agent that permits the covalent attachment of collagen I, which is a suitable substrate for the growth of epithelial cells. The presentation will describe the characterization of the polymer physics and a possible mechanism for the strength enhancement and will describe the efforts toward development of an artificial cornea.

COLL 35 Biomolecule/nanoparticle hybrid systems on surfaces for sensor, circuitry and device applications

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The comparable dimensions of biomolecules and metallic or semiconductor nanoparticles (NPs) suggest that the generation of biomolecule/NP hybrid systems may combine the catalytic and selectivity features of biomolecules with the unique electronic and optical properties of NPs. The use of biomolecule/NPs hybrid systems for sensor applications will be addressed with several examples: 1) The reconstitution of apo-enzymes on cofactor-modified Au NPs associated with electrodes is used to electrically contact the enzymes and to develop amperometric biosensors. 2) Nucleic acid-functionalized semiconductor NPs and redox-protein-modified semiconductor NPs are used for the optical or photoelectrochemical detection of DNA or the activity of enzymes. Biomolecule/NP hybrid systems may act as building blocks for nanoscale circuitry and devices. The examples that will be discussed include: 1) The design of patterned actin-Au nanowires and their use as ATP-driven nanotransporter. 2) The use of metal-NP-modified redox enzymes as “biocatalytic inks” for the formation of metallic nanowires on surfaces. 3) The use of nucleotide-modified metallic or semiconductor NPs as functional nanostructures for the assembly of nano-circuitry or nano-devices on surfaces.

COLL 36 Influence of the size of gold nanoparticles on adsorption, conformation and binding activity of antibody molecules

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There have been significant interests in using nano-sized objects for biological and medical application due to their unique size-dependent physical and chemical properties. One of the most attractive research fields is nanoparticles in conjugation with antibodies, which possess remarkable recognition capabilities and can be used in many biomedical applications. In this study, the size influence of gold nanoparticles on the adsorption, conformation and binding activity of adsorbed monoclonal antibody (anti-CD20) molecules was investigated by fluorescence microscopy, circular dichroism and fluorescent-activated cell sorting. The combination of these techniques can give complementary relationship between adsorption-induced changes in antibody conformation and binding activity. At the saturation coverage, the change of the secondary structure of anti-CD20 from the native conformation is less when it is adsorbed to smaller size nanoparticles. The conformation change subsequently affects the targeting ability of the antibody molecules, as the FACS result shows that a lower degree of cell binding activity when anti-CD20 is adsorbed to larger size nanoparticles. These results show that the nanoparticle size is a critical factor in determining the effectiveness of nanoparticle-antibody conjugates in biological applications.

COLL 37 Functionalised nanoparticles as novel biosensing materials

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Metallic nanoparticles can be used as basic materials for a wide variety of purposes including building blocks for nanoassemblies, substrates for enhanced spectroscopies such as fluorescence and Raman and as labels for biomolecules. Here we report how silver and gold nanoparticles can be functionalised with specific biomolecular probes to interact in a specific manner with a target molecule to provide a change in the properties of the nanoparticles which can be measured to indicate the molecular recognition event. Examples of this approach that will be discussed include DNA hybridisation to switch on surface enhanced resonance Raman scattering (SERRS) when a specific target sequence is present, recognition of specific proteins by aptamer functionalised nanoparticles by surface plasmon resonance and SERRS and use of nanoparticles functionalised with antibodies to provide a new type of immunoassay. These examples indicate how nanoparticles can be used to provide highly sensitive and informative data from a variety of biological systems when used with optical spectroscopy.

COLL 38 Bio-nanoparticle conjugates for the acquisition of forensic evidence

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The aim of this research is to obtain “intelligence” information from latent fingerprints to aid police, and other security forces, with their investigations. To achieve this goal we are devising bio-nanoparticle conjugates which bind to metabolites excreted in the sweat and deposited with a

fingerprint. Pre-formed gold nanoparticles are formulated though the citrate reduction of a gold salt using the "Turkevich" method. The biological recognition molecule is then self-assembled to the particles to form conjugates of ca. 16 nm in diameter. A solution of the nanoparticle conjugates is incubated with the forensic evidence. Following interaction between the bio-nanoparticle conjugates and the metabolite the presence of the target metabolite is detected using fluorescence microscopy. The fabrication and the successful application of this technology will be presented.

COLL 39 Water-dispersible fluorescent nanospheres for applications in fluorescent in-situ hybridization assays

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A new strategy for the preparation of water-dispersible spheres that are smaller than 50 nm and contain a large number of covalently-bound dye molecules is to be reported. Specifically, such nanospheres are prepared starting from a diblock copolymer poly(tert-butyl acrylate)-block-poly(2-hydroxyethyl methacrylate) or PtBA-PHEMA. This is achieved by first reacting the hydroxyl groups of PtBA-PHEMA with succinic anhydride to introduce some carboxyl groups into the PHEMA block. Such carboxyl groups are then reacted with Texas-red cadverine (TX-NH2) to incorporate the dye molecules. The TX-bearing diblocks formed spherical micelles in block-selective solvent DMF/toluene containing 2% DMF. "Permanent" micelles or nanospheres are prepared after crosslinking the TX-bearing PHEMA core block. Such nanospheres are made water-soluble by cleaving the tert-butyl groups from the PtBA coronas. Water-soluble nanospheres with many TX groups and a high TX fluorescence quantum yield may find applications fluorescent in-situ hybridization assays.

COLL 40 Cancer nanotechnology: Designing multifunctional nanostructures for targeting tumor cells and vasculatures

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Significant progress has been made in developing new agents against cancer and in formulating them for in-vivo delivery and targeting. Research in genomics and proteomics continues to uncover biomolecular signatures (biomarkers) that are unique to cancer development and progression. Yet, the major challenge to target and selectively kill cancer cells remains. Linked with targeting moieties such as tumor-specific ligands or monoclonal antibodies, nanoparticles can be used to target tumor cells and tumor vasculatures. We have attained dramatic in vivo tumor shrinkage and tumor vasculature disruption using ternary biomolecular nanostructures. For hydrophobic anti-cancer agents not amenable to chemical conjugation, we have used the principles of molecular self-assembly to engineer targeted nanoparticles. These nanoparticles are also applicable to delivery and targeting of diagnostic and imaging agents. In particular, bioconjugated quantum dots make it possible to track movement of individual labeled molecules inside a cell or a small number of cancer cells growing in a living animal. The ability to design multifunctional nanostructures has opened new opportunities in early cancer diagnostics, molecular profiling, and integration of cancer therapy and imaging.

COLL 41 Biomimetic DNA compaction by cationic nanoparticles

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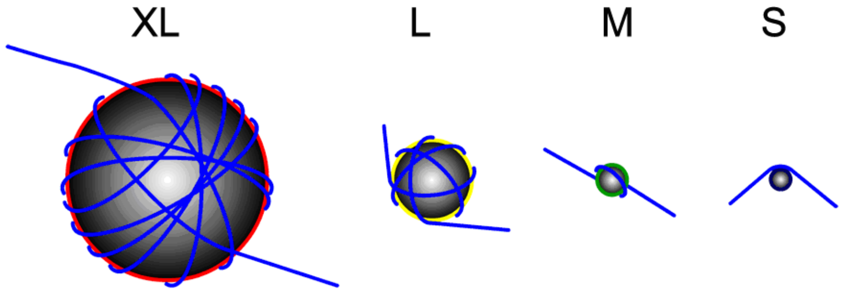
We have designed a system which consists of long DNA interacting with cationic nanoparticles (NP) with diameters 10 (S), 15 (M), 40 (L) and 100 nm (XL) to mimic in vivo DNA compaction into chromatin. DNA compaction by NP is stepwise and progressive, proceeds through the formation of beads-on-a-string structures, and, similarly to DNA-histone interaction, is optimal at a physiological salt concentration. There are three distinct mechanisms of DNA compaction.



In the case of large nanoparticles (XL and L), DNA chain is freely adsorbed electrostatically on the positively charged nanoparticle surface. When size of nanoparticle becomes smaller (M), rigidity of DNA chain becomes a critical factor, and DNA compaction proceeds though DNA chain wrapping around nanoparticles, which remarkably mimics DNA packaging by histone particles in vivo. In the case of even smaller particles (S), DNA chain cannot bend sufficiently to wrap around cationic nanospheres, and nanoparticles decorate DNA chain.

COLL 42 Turnip yellow mosaic virus as a chemo-addressable bionanoparticle

Hannah Barnhill, Venkata S. Kotakadi, Fang Xie, and Qian Wang, Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC 29208, barnhill@mail.chem.sc.edu

It has been demonstrated that bionanoparticles (i.e. viruses, ferritins and protein cages) are useful scaffolds for nano-based materials. We have studied the reactivity of turnip yellow mosaic virus (TYMV) and demonstrated that without further genetic modification, the lysine and carboxylic acid residues can be specifically and independently addressed. The TYMV lysine residues were reacted with a series of N-hydroxy succinimidyl esters and it was found that up to 90 lysines can be modified. The virus is stable to the reactions and the attached molecules and remains intact as shown by FPLC and TEM. The carboxylate residues on TYMV (i.e. aspartate or glutamate) are also reactive with propargyl amine via EDC coupling. The carboxylate residues can then be further modified using the fluorogenic [3+2] cycloaddition of coumarin azides and alkynes. A fluorescent product was detected and TYMV remained intact after the reaction in contrast to other bionanoparticle systems.

COLL 43 Chemistry of biological adhesion

Deborah E. Leckband, Department of Chemical and Biomolecular Engineering, University of Illinois, 600 S. Mathews Avenue, Urbana, IL 61801, Marco Bayas, Departamento de Física y Astronomía, Escuela Politécnica Nacional, Alice Kearney, Sir William Dunn School of Pathology, University of Oxford, and Anton van der Merwe, Sir William Dunn School of Pathology, Oxford University

Intercellular adhesion in tissues is determined primarily by large numbers of protein binders on cell membranes. A fundamental question is how bond chemistry determines the adhesive strength of intercellular junctions. While much is known about the strengths of single bonds, cell adhesion is rarely mediated by single proteins. Yet no current analysis predicts how molecular properties scale the collective adhesive behavior of multiple bonds in parallel. This talk describes a multi-scale investigation of the adhesive strength of multiple protein bonds in parallel and the relationship to their thermodynamic and kinetic properties. Atomistic simulations identified adhesion protein

mutations that generated different bond properties. Subsequent force measurements with these protein mutants established correlations between their thermodynamic and kinetic properties and the measured adhesion between membranes bridged by the proteins. These findings suggest surprising similarities between the strengths of single bonds and the strength of adhesion due to multiple bonds acting in parallel.

COLL 44 Mapping the interaction forces between TAR RNA and TAT peptides on GaAs surfaces using chemical force microscopy

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The complexation of the HIV transactivation response element (TAR) RNA with the viral regulatory protein TAT is of enormous interest for the design of new sensing and therapeutic strategies. In this work we anchored TAT peptides on GaAs surfaces using microcontact printing. Atomic Force Microscopy was used to quantify the interaction between TAR RNA and model TAT peptide sequences. Different pH conditions were utilized in order to assess specific vs. non-specific interactions. AFM tips functionalized with TAR RNA molecules were used to collect adhesion maps that displayed stronger interaction with peptide sequences that contained a greater number of arginine residues. All of the studies consistently showed a pH dependence of the interaction between the surface bound peptides and the TAR RNA on the AFM tips. This work quantifies the TAR RNA / TAT peptide interaction at the single molecule level. The conclusions in this paper are consistent with previous work and demonstrate that cationic residues are responsible for the polyelectrolyte-like affinity of TAT peptides for TAR RNA.

COLL 45 Nanomechanical motion from microcantilevers as a platform for detecting phase changes of macromolecules

Sibani Lisa Biswal[1], Digvijay Raorane[1], Alison Chaiken[2], and Arun Majumdar[1]. (1) Department of Mechanical Engineering, University of California, Berkeley, 6186 Etcheverry Hall, Berkeley, CA 94720, sbiswal@berkeley.edu, (2) HP Labs

We describe the development and use of microcantilevers as a sensitive platform for the study of thermal stability of macromolecules. The sensitivity of these cantilevers combined with their fast response time has allowed us to use these sensors for the thermal analysis of phase transitions.

The microcantilevers based sensors directly translate changes in Gibbs free energies due to analyte-surface interactions into mechanical responses. In these cases the cantilever will bend thereby transducing a biochemical signal into a mechanical one. One can follow surface processes by measuring the bending of a cantilever. We have been able to utilize this phenomenon to study phase changes in a material while scanning the sample temperature. With the microcantilevers, we are able to explore the stability of DNA under a variety of solution conditions. Differences in the lengths and intermolecular interactions between single and double stranded DNA are highlighted by variations in cantilever deflection. This technique has allowed us to probe of DNA melting dynamics, which allows us to better understand the stability of DNA complexes on surfaces.

COLL 46 Nanoscale dielectrophoretic spectroscopy of Erythrocytes *in situ*

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The dielectrophoretic properties of red blood cell surface have been imaged with nanoscale resolution using dielectrophoretic force microscopy. Dielectrophoresis, the frequency dependent force between a polarizable particle in a non-uniform electric field and a polarizing electrode, has been coupled with the feedback mechanism of an atomic force microscope in a novel spectroscopy technique. The application of a radio frequency alternating electric potential to a conductive scanning probe generates a large non-uniform field at the apex of the probe. Objects in the vicinity of the varying electric field will experience a force that depends on the waveform applied to the probe and the frequency dependent dielectric properties of the substance. The dielectrophoretic spectrum of the surface can be measured with nanoscale resolution by monitoring the resulting forces upon the probe when the waveform applied to the probe is varied in frequency. In addition to probing molecular structure with dielectrophoretic spectroscopy, when the dielectric properties of a substance are known a priori, the application of a constant frequency waveform leads to a short range interaction between the surface and the probe that can be used to preform non-contact imaging in solution.

COLL 47 Novel antifreeze proteins and their interaction with the ice crystal

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One promising approach in improving the survival of cells after cryopreservation is by using antifreeze proteins (AFPs) as an additive. AFPs have been shown to allow organisms to survive at temperatures below the freezing point of their body fluids by adsorbing to the ice crystal and inhibiting its growth. Recently, there is a considerable attention due to their potential applications. In this study, we expressed novel AFPs and characterized them by using our homemade osmometer. Thermal hysteresis measurements were carried out to verify the activity of the newly expressed proteins. In addition, the ice crystal growth rates and geometry for the different AFPs were compared. The relationship between the protein structure and the activity of different proteins will be presented.

COLL 48 Peptide adsorption thermodynamics on nanothin polymer films

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This contribution describes experimental measurements of submolecular-level interaction energies involved in the process of peptide adsorption on polymer films using surface plasmon resonance spectroscopy. Gibbs energy change on adsorption (ÄGad) for tyrosine, phenylalanine, and glycine homopeptides were measured at 25 °C and pH 7 on highly uniform, nanothin polymer films, and the results were used to predict ÄGad for homologous homopeptides with a larger number of residue units, as well as for a mixed residue peptide. Nanothin poly(2-vinylpyridine), poly(styrene) and poly(1-benzyl-2-vinylpyridinium bromide) films were used for the adsorption studies; they were prepared using a graft polymerization methodology. In-situ swelling experiments were done with ellipsometry to examine the uniformity of the surfaces and to ensure that the graft densities of the different polymer films were similar to facilitate the comparison of adsorption results on these surfaces.

COLL 49 Engineering and assembly of zeolite nanoparticles: From chips to fuel cells

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Zeolites are crystalline oxides with uniform nanometer-sized pores. At present, zeolites are commercially used as catalysts and separation media, and for both applications, they are used in powder composite form from micrometer-sized zeolite particles. We have recently demonstrated that zeolite nanoparticles can be used as building blocks via self assembly for hierarchically porous structures with designed macro-morphology, and for functional films. In this presentation, the engineering of zeolite nanoparticles will be discussed for their applications as low dielectric constant (low-k) films for future generation computer chips and acid functionalized zeolite nanocomposite membranes for fuel cells.

COLL 50 Nano-crystalline titania films with orthogonally aligned nanopore arrays

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The amorphous walls and electrically insulating nature of surfactant templated mesoporous silica films limits their applications to fields such as separations and low-k dielectrics. Transition metal oxides like titania which have crystalline walls are excellent alternatives for photovoltaic, catalytic and electron applications. Non-interconnected 2D hexagonally close packed (HCP) cylindrical channels would be ideal pores for many applications, but they usually align parallel to the substrate surface, and are inaccessible. We have aligned cylindrical pores in silica films normal to the substrate by dip coating films onto chemically neutral substrates. Here we extend this idea to create crystalline titania films with orthogonally oriented HCP cylindrical mesopores. This is challenging because crystallization destroys long range order even when the pores are oriented parallel to the surface. Controlling processing factors like humidity and calcination temperature allows us to preserve orthogonally oriented HCP pores in titania films useful for applications such as photovoltaics.

COLL 51 Photophysical study of solvation at liquid-zeolite interfaces

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This report describes the behavior of arene photosystems in the cavities of the zeolite Faujasite interfaced with bathing polar solvents. Retention of arenes in zeolites is described in which the arene is placed in zeolite cavities by adsorption from solution but cannot be extracted with desorbing polar solvents such as methanol. The microenvironment of retained species in polar-solvated zeolite cavities is described through fluorescence probing of polarity and rigidity. Accessibility of retained species to solutes in the solution bathing the zeolite is described from studies of excited state quenching processes. The results of this study show unique solvation in the confined space of zeolite supercages. The medium description is highly dependent on the chemical properties of the zeolite, be it ionic or hydrophobic.

COLL 52 Controlling zeolite morphology using oil/water/surfactant mixtures

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This talk will summarize our recent efforts to synthesize zeolite crystals with controllable morphology using oil/water/surfactant/mixtures. The first part of the talk will summarize silicalite-1 growth in oil/water/surfactant mixtures at low temperatures (<368 K). Clear differences are observed between the crystals formed in nonionic microemulsions [1,2] and syntheses using ionic surfactants [3,4]. The crystal morphology depends on the nature of the surfactant, and control experiments clearly show that surfactant adsorption on the growing crystal surface, not the confined space afforded by the microemulsion is central to the crystal habit obtained. The second part of the talk will highlight recent work on the growth of zeolite LTL rods, [5] a zeolite with a Si/Al ~ 1.5. In the presence of both cationic and nonionic surfactant/oil/water mixtures crystals that are highly anisotropic (L/D ~ 5 – 10 typically, with values as high as 45 observed) are formed, in contrast to the normal synthesis (L/D ~ 1.5 – 2). Given their high extra-framework cation density these materials appear to be promising candidates for the growth of nanowires arrays in the zeolite pore system.

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COLL 53 Silica nanoparticles: Structure, stability and their role in materials synthesis

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The microstructure of silica in basic aqueous solutions containing organic cations and prepared from monomeric precursors is reviewed and interpreted within the context of classical ideas of self-assembly of molecular aggregates. The silica nanoparticles frequently observed in these systems have a core-shell structure with silica in the core and the organic cations at the shell. Individual particles are observed when the forces between particles are repulsive—as is the case for small cations such as tetramethylammonium or tetrapropylammonium—and extended structures such as M41S materials are formed when the forces are attractive—as is the case for surfactants such as cetyltrimethylammonium. Although at room temperature the silica and the organic cations are segregated, upon heating the organic cations are embedded within the particles. This transformation signals the onset of the process of structure direction whereby the size and geometry of the organic cation induce changes in the structure of silica that may lead to zeolite nuclei.

COLL 54 Self-assembly synthesis and structural properties of ordered mesoporous silica fibers

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The ability to synthesize nanostructured inorganic materials with controlled microstructural and morphological features will provide materials with unique characteristics in unprecedented ways. One application of this group of materials is in nano-reactors for the extrusion of high quality polyethylene (PE) fibers. This paper will discuss self-assembly synthesis of ordered mesoporous silica with controlled microstructures and desirable shapes. The template-assisted growth of mesoporous silica under acidic and quiescent conditions at an oil-water interface can generate mesostructured silica at the interface with fibrous, gyroidal, spherical, and film morphologies. Synthesis conditions can be used to alter the growth environment and control the product morphology. Fiber morphology is obtained at narrow range of experimental conditions due to slow and one dimensional diffusion of silicon alkoxide through the interface. Variation in these conditions can alter the axial growth of silica and yield non-fibrous shapes. The fibers grow from their base attached to the interface and coalesce to form fibers with larger diameters. Adsorption and diffusion of carbon dioxide and ethylene in the ordered mesoporous silica fibers were studied by a gravimetrical method. Gas transport in the mesoporous silica fibers is governed by combination of Knudsen and surface diffusion mechanisms. Surface diffusion contributes to 40% of the net flow reflecting a highly smooth pore surfaces. Real Knudsen and surface diffusivities are in the order of 10-3 and 10-5 cm2/s respectively. The one-dimensional mesopores are 45 time longer than the macroscopic fiber length and align helically around the fiber axis with a pitch value of 1.05 micron.

COLL 55 Self-assembly of rodlike nanoparticles

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We characterize the self-assembly of anisotropic rod-like nanoparticles observed on a TEM grid, by calculating the extent of orientational and positional order present in the patterns typically formed by evaporating the solvent. The drying process is accompanied by complex hydrodynamic and thermodynamic events, which create the rich range of patterns observed. Being anisotropic in shape, the rods can form liquid crystalline assemblies above a certain concentration, and this manifests in presence of nematic-like and smectic-like assemblies observed by several groups. We calculate the order parameters extracted from the various assemblies observed, and compare and contrast the observed phase behavior to the one expected on basis of theory and simulations.

COLL 56 Control of surface spacing between functionalities at sub 10-nm level for biological application

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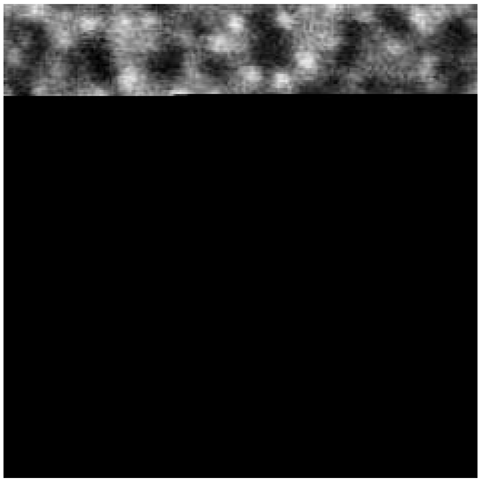
We have studied ways to control surface spacing among functional groups. Considering the sizes of biomolecules, we have been keen on generating spacings of a few nm (up to tens of nm), and have tried to eliminate lateral steric hindrance by immobilizing individual biomolecules specifically on a particular functionality. For example, self-assembly of a dendron of appropriate generation provided mesospacing (ca. 3-10 nm) between reactive functional groups on the surface. A study of the behavior of a short oligonucleotide on the surface revealed that very high single nucleotide polymorphism discrimination efficiency (100: <1) was achieved, comparable to that observable in solution. In extension, we observed that surfaces with patterns controlled at the nanoscale were very useful for DNA microarrays. Control of surface spacing at sub 10-nm scale is at present primitive, lacking long-range regularity, but it already has shown unusual efficacy in some biological applications.

HRSEM image (50 nm x 50 nm) after tethering gold nanoparticles at the apex of the immobilized second generation dendron.



COLL 57 Integration of self-assembling block copolymer materials into the lithographic process

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We investigate materials and processes for advanced lithography in which self-assembling block copolymers are integrated into existing manufacturing processes for patterning ultra high resolution structures that are useful for the fabrication of microelectronic devices. We aim to develop block copolymer lithography to achieve 10 nm resolution and retain the essential attributes of current manufacturing practices: pattern perfection, low line edge roughness, precise dimensional control, placement of the structures, including registration and overlay with nanometer precision, the ability to pattern geometries for device fabrication, and the ability to pattern substantially different features sizes in one layer. We anticipate that this technology may be suitable for insertion at the 45 nm node and be scalable to 10 nm and below.

COLL 58 In-Plane electrochemical potential gradients for active spatiotemporal control of molecular composition and physical properties

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Spatially graded physical structures are of interest, because molecular composition and physical properties can be continuously varied in space. We are working to build laterally anisotropic surfaces and thin films in which the interaction with the surrounding medium can be tuned as a function of position and time by applying a voltage, and also to understand how these structures may be used to recognize and capture fluid-borne adsorbates/analytes. Specifically we are developing surfaces in which designed lateral variations in chemical properties, *e.g.* adsorption, ligation, etc. are established without changing the nominal composition of the surface. These goals are being realized by coupling in-plane potential gradients to environmentally-responsive systems/structures (ERS) prepared from multi-component acrylate-based polymers (hydrogels) and composite ERS structures in which the hydrogels are decorated with ligand-bearing metallic nanoparticles. To zeroth order the lower bound on spatial resolution in these structures is dependent on the resistivity of the material in which the electrochemical gradient is established and the magnitude of the potential gradient, although the resolution can be improved, for example, by coupling to non-linear surface phenomena, such as nucleated growth. Extensions of the general approach to arbitrary two-dimensional distributions and nanoscale gradients will be discussed.

COLL 59 Patterning, templating, and self-assembly by nanocomponent hybridization to 2-D DNA scaffolding

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An approach for ultra high resolution patterning, templating, and self-assembly based on in situ hybridization of nanocomponents to 2D DNA scaffolding is described. The DNA scaffolding was formed from a set of 21 oligonucleotides that assemble into a 2D crystal containing rows of ssDNA attachment sites. Au nanoparticles (5 to 10-nm) were coated with ssDNA complementary to the scaffolding attachment sites, suspended in solution, and deposited on a pre-assembled DNA scaffolding attached to a surface. The nanoparticles self-assembled into rows with a 64-nm inter-row spacing controlled by the DNA scaffolding design. The interparticle gap, which was independently controlled by the DNA shell design, was intentionally varied from 2 to 15 nm. Sequence-encoded self-assembly of alternating rows of different sized nanoparticles (5 and 10-nm) was also demonstrated. This approach facilitates the patterning of substrates, the templating of surface structures, and the self-assembly of objects – with nanometer-scale precision.

COLL 60 Scaffolded DNA origami for nanoscale shapes and patterns

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A key goal for bottom-up nanofabrication has been to generate structures whose complexity matches that achieved by top-down methods. Towards this goal, DNA nanotechnology provides an attractive route. Here I describe a method for folding long single strands of DNA into arbitrary two dimensional shapes using a raster fill technique. Self-assembled in a one-pot reaction from the 7 kilobase genome of phage M13mp18 and over 200 synthetic oligonucleotides, the resulting structures are roughly 100 nm in diameter. Experimental structures approximate desired shapes, such as a 5-pointed star, with 6 nm resolution. At the same resolution, structures can be decorated by arbitrary patterns such as words or images. Enabled by a program for laying out complicated designs and using inexpensive unpurified oligonucleotides, this method helps move DNA nanotechnology from the realm of research towards that of engineering.

COLL 61 Biomolecular nanolithography: Using DNA to direct nanoparticle assemblies

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One of the current challenges in developing nanoparticle-based devices is to control the placement of nanoparticles on surfaces. Previously we have shown that, in solution, Au-nanoparticles functionalized with a cationic ligand shell self-assemble on the negatively charged backbone of DNA. These particles close-pack along the DNA, so nanoparticle spacing can be precisely tuned by the appropriate choice of ligand shell. Here we report the assembly of parallel, linear arrays of 1.5 nm Au-nanoparticles on a thermally grown SiO_2 surface by aligning DNA on SiO_2 prior to decorating the DNA backbone with nanoparticles. Using specially fabricated SiO_2 TEM grids, we are able to quantify the effects of assembly conditions, and show that nanoparticle core size and spacing can be conserved. Furthermore, we are able to contact these arrays with 5-µm electrode gaps. These devices show nonlinear electron transport at room temperature with a temperature dependence consistent with Coulomb blockade.

COLL 62 Depletion attractions and design of nanostructured polymer materials

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In 1985 A. Gast predicted that particles protected by tethered polymer layers attract when suspended in solutions of long polymer chains and repel when solution chains are short. Some twenty years later this understanding of such depletion-like entropic interactions found some surprising applications in conception of polymer materials structured on submicron or nanometer scale. I illustrate the importance of controlling depletion entropic interactions in building up versatile and potentially low cost strategies for two classes of self-assembled systems: super-tough plastics reinforced by copolymer dispersions and nanostructured bicontinuous materials made by reactive blending of industrially available polymers.

COLL 63 Dynamics of diblock copolymers at polymer/polymer interfaces

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For the first time, we study the dynamic concentration profiles of an AB diblock co-polymer (i.e., the surfactant) at A polymer/ B polymer interfaces. We create thin polymer films containing two surfactant-bearing polymeric interfaces and follow the transient concentration profiles of the diblock copolymer by dynamic secondary-ion mass spectroscopy (SIMS). Transport of the diblock copolymer depends on the two binary Fickian diffusion coefficients and on the depth of the thermodynamic potential well that holds the surfactant molecules at the interface. Polymer equilibrium parameters are determined by independent SANS and gel-permeation-chromatography measurements. Diffusion coefficients are measured in independent SIMS experiments. We find excellent agreement between the measured transport rates of the AB surfactant across the A/B film interfaces and those calculated using a SCFT free-energy profile and diffusion in a potential field. Fascinatingly, no kinetic barriers to adsorption/desorption are found.

COLL 64 Advancing nanofabrication with small angle scattering and reflectivity measurements

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As feature sizes in microelectronic devices continue to decrease towards sub-50 nm dimensions, new measurement methods are needed to characterize the device structure and to understand the physical phenomena that may limit their fabrication. Neutron and x-ray beams are powerful probes of structures having characteristic length scales ranging from (1 to 1000) nm in thin films and in the bulk. In particular, X-ray reflectivity (XR), neutron reflectivity (NR), small angle neutron scattering (SANS), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy can be applied in novel ways to understand fundamental issues important to the fabrication of nanoscale structures in the microelectronics industry and in other applications. In this talk, we demonstrate the application of these measurement methods to investigate critical problems in the development of photoresist materials used in photolithography and of nanoporous low-dielectric-constant materials needed for next generation integrated circuits.

COLL 65 Effect of magnetic nanoparticle aggregates on block copolymer morphology

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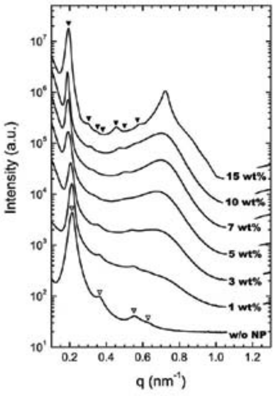
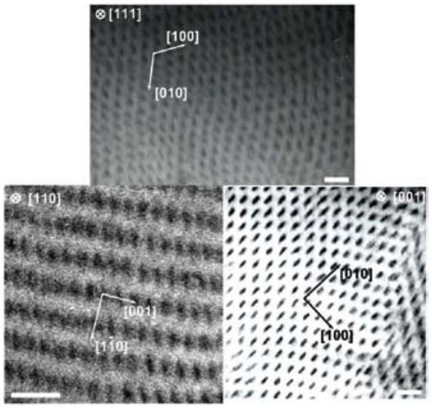
We investigate the effect of magnetic nanoparticle (NP) aggregates on the ordered morphology of block copolymers by varying NP concentration. Monodisperse γ-Fe2O3 NPs with surfaces modified with oleic acids have been synthesized and PS-b-PI diblock copolymers showing cylindrical morphology were used as a mixing component against the NPs. With the increase in NP concentration, domains of NP aggregates were observed. It is surprising to note that regular lattice-like aggregates with γ-Fe2O3 NPs induce the intriguing morphological transformation from hexagonal cylinders to body-centered cubic spheres of the block copolymer via undulated cylinders. We also demonstrate the preferred orientation of anisotropic microdomains of PS-b-PI, which is known to be difficult to orient by applying an electric or a magnetic field, and the epitaxial morphological transformation in the presence of magnetic NP aggregates. This result could add more flexibility in the structural control and the orientation of block copolymers opening up new applications in the future.





COLL 66 On the assembly of micelles and colloidal particles

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Micelles and colloidal particles respond to electromagnetic fields in various ways. With micelles, such fields give rise to van der Waals interactions and we show how anisotropic interactions align micellar structures with the underlying crystal. With colloidal particles, externally applied fields alter the structure of polarization layers and engender hydrodynamic interactions that attract particles towards one another thus producing colloidal crystals. The presentation will survey the underlying theory and experimental confirmation.

COLL 67 Solution synthesis of complex nanostructures from silica nanowires templates

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We have synthesized silica nanowires from which various nanostructures are derived. The surface of the silica nanowires is functionalized for the construction of these nanostructures. In one example, we have decorated these nanowires with gold and silver nanoparticles, and have controlled the coverage through the selection of surfactants and environmental pH. In another example, iron oxide nanoparticles are coated on the surface of these nanowires. The results of these syntheses will be presented and the application potentials of these nanostructures, which behave like macromolecules in solution, will be discussed.

COLL 68 Biomolecular functionalization and organization of nanoparticles

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Our work is focussed on the DNA-functionalization of proteins and nanoparticles. For instance, we have developed self-assembled oligomeric networks comprised of streptavidin, gold nanoparticles and DNA, which are applicable as reagents in ultra-sensitive protein detection assays, as building blocks for switchable biomaterials, or as nanometer-scaled *soft material* standards for scanning probe microscopy. Moreover, conjugates of single-stranded DNA and STV have been utilized as biomolecular adapters for the immobilization of biotinylated macromolecules at solid substrates via nucleic acid hybridization. This *DNA-directed immobilization* allows one for reversible and site-selective functionalization of solid substrates with metal and semiconductor nanoparticles, or, vice-versa, for the DNA-directed functionalization of nanoparticles with proteins, such as immunoglobulins and enzymes. Moreover, covalent DNA-protein conjugates allow for selective positioning of functional protein along a single-stranded nucleic acid molecule. Examples include the fabrication of functional hybrid nanostructures from metal and semiconductor nanoparticles, nucleic acids and proteins, enabling for applications in biosensing, materials science and as catalysts in organic synthesis.

COLL 69 Plant viruses based self-assembly and cell-binding study

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Plant viruses represent very stable and beautiful self-assembled architectures at the nanometer level. We will report our recent progress in the self-assembly and the materials application of spherical and rod-like viruses. Turnip yellow mosaic virus and tobacco mosaic virus have been selected as prototypes in the study. Their three dimensional structures have been characterized at near atomic resolution, and their composition and surface properties can be controlled using molecular biology techniques combining with chemical modification. The self-assembly of both viruses can be controlled to form well-ordered 1D, 2D and 3D structures. In particular, the assembly of chemically and genetically-tailored bionanoparticles at the interface between immiscible fluids results in large scale ordered 2D arrays. The chemical, physical, dynamical and mechanistic aspects of these assemblies have been studied; and the virus-based arrays have been used in the cell-adhesion and cell-migration studies.

COLL 70 Nanoparticle-DNA conjugates bearing specific number of short DNA strands by enzymatic manipulation of nanoparticle-bound DNA

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Among the biomolecules that used in nanoparticle modification, DNA is no doubt one of the most commonly used linker molecules, because of its unique recognition capability and enzyme processibility. This study reported our new approach of generating gold nanoparticle-DNA conjugates bearing specific number(s) short DNA linker molecules that can be used as building blocks to construct nano-assemblies or as nanoprobes for quantitative gene detection. Gold nanoparticles bearing specific numbers (1, 2, 3, 4, 5 or 6) of single-stranded DNA less than 20 bases were obtained using the combined methods of gel electrophoresis and DNA digestion. As the number of DNA strands on the nanoparticles is well-defined, the hybridization ability of such conjugates with different targets, such as complementary and single nucleotide mismatch DNA can be quantitatively investigated. Preliminary results show a 80% hybridization efficiency with complementary DNA. Using fluorescent labeled DNA as the target, the conjugates bearing different number of DNA strands exhibited distinct different hybridization signals, indicating the possibility for quantification purposes. The enzyme digestion efficiency of nanoparticle-bounded DNA was also studied and a digestion efficiency as high as 92%, which is very close to the free DNA digestion.

COLL 71 From single to multienzyme assemblies: Do enzymes sleep and work?

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Enzymes in their natural environment, the cell, often interact with numerous neighbouring proteins, and their catalytic activity generally depends upon their environment and their role in the catalytic cycle. Towards studying this enzymatic synergy we have synthesized a variety of enzyme architectures constructed from enzyme giant amphiphiles,[1] and enzyme containing nanoreactors constructed from polymersomes.[2,3] During these investigations the direct and real time observation of a single-enzyme-catalyzed reaction was studied using confocal fluorescent microscopy (CFM).[4] This study allowed us to unravel hidden characteristics in the catalytic behavior of a single lipase, which were interpreted using a fluctuating enzyme model.[5] In addition we have developed a variety of hetereo- and homo-dimers in which enzymes are ‘clicked together or to a Bovine Serum albumin (BSA), which acts a protein foot. Single enzyme studies of these systems revealed a substantial synergistic behaviour, and a clear enzyme memory effect.

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COLL 72 Assembly of functional DNA-multiprotein complexes at nanoscale

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Directed, biologically-driven self-assembly has the potential to yield hybrid multicomponent architectures with applications ranging from sensors and diagnostics to catalysts and responsive materials. To enable these applications, it is critical to gain control over the precise orientation and geometry of biomolecules interacting with one-another and with surfaces. Such control has thus far been difficult to achieve in even the simplest biomolecular designs. We report a general methodology for the design and synthesis of functional, oriented, and reversibly switchable hierarchical assemblies at the nanoscale using DNA-protein and protein-protein interactions. The biomolecular assembly relies on the highly selective recognition between transcription factors (TFs) and their cognate DNA motifs that serve as transcription factor binding sites (TFBSs) along with the calmodulin-calmodulin binding peptide interaction that is regulated by Ca2+. Through these two types of controllable interactions, we achieved the sequential and hierarchical self-assembly of multiprotein complexes complete with embedded fluorescence and catalytic functions, which may serve as a paradigm for multifunctional assemblies.

COLL 73 Enzymatic manipulation of surface biomolecular nanostructures for the detection of bioaffinity interactions with SPR imaging and fluorescence measurements

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Surface bioaffinity measurements rely on the optical detection of the formation of surface biomolecular nanostructures of DNA, RNA, proteins or antibodies. The simplest of these surface bionananostructures include surface bound DNA-DNA and DNA-RNA duplexes, protein-peptide conjugates, and carbohydrate-lectin complexes. The formation of all of these surface biostructures can be detected with various surface-sensitive optical techniques such as surface plasmon resonance imaging (SPRI), surface plasmon fluorescence spectroscopy (SPFS). The specificity and sensitivity of these optical bioaffinity sensing measurements can be enhanced with the enzymatic manipulation of the surface bionanostructures formed upon biopolymer adsorption. For example, we have recently demonstrated the use of the enzyme RNase H in conjunction with RNA microarrays for the ultrasensitive SPRI detection of DNA. This talk will describe a number of novel surface enzymatic methods (e.g., surface ligation, polymerase and protease) for the processing of surface bionanostructures for enhanced bioaffinity sensing applications.

COLL 74 Foldamers with hybrid biological and synthetic sequences as selective DNA fluorescent probes

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Our most powerful architectural motif for the study of bio-molecular interface is based on self-assembling amphiphilic foldermers with alternating single-strand DNA sequences and planar conjugated perylene units, which were found to self-organize into folded nanostructures. Upon this observation, hybrid foldermers have been readily developed for DNA detection. The strategy is that organic chromophores emitting different color fluorescences are used to replace perylene as signal part incorporated with specifically designed ssDNA --- special versions of the perylene foldermers as probes. Thus a series of D-A-D, D-π-D, A-π-A, and D-π-A conjugated molecules was designed, synthesized, and embeded to form foldamers via DNA synthesizer. The rationale here is that when the built-in DNA sequences in the hybrid folermer complement with the target DNA in completely match or partially match situation, the originally formed nanostructures of the signal part will be destroyed to such an extent that the color change of the foldermer can be detected like encoded FRET probe. Different mismatching DNA sequences are leading to different color emissions due to the different levels of FRET between the chromophores. In view of the skeleton, unlike molecular beacons which usually have organic dyes at both ends of DNA sequences, our hybrid foldermers have

the organic dyes inserted alternately between the DNA sequences and end up by the specially designed DNA sequences with active bio-functions which allow further biological manipulation. The structural specialization makes our foldermers the unique and perspective candidates for DNA detection.

COLL 75 Gold nanostructures for DNA conjugation and radiation enhancement

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We have demonstrated that nanoparticles conjugated to DNA can enhance the effect of ionizing radiation in DNA single and double strand breaks (SSB and DSB). In order to achieve the maximum enhancement of radiation effect, we have synthesized complex gold nanostructures from gold nanoparticles that are both DNA binding and water soluble. Furthermore, these nanostructures only contain neutral surfactants to allow easy passage of Auger electrons and radicals moving from gold nanoparticles to DNA. Specifically, ethidium thiol ligands and water soluble ethoxy ligands covered gold nanoparticles are synthesized. These nanostructures are then conjugated to supercoiled DNA. Results of conjugation and radiation studies with atomic force microscopy, transmission electron microscopy, photoluminescence, and gel electrophoresis will be presented.

COLL 76 Decoupled gel to fluid phase transitions in supported phospholipid bilayers

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Bilayer films of phospholipids supported on solid substrates are of great interest as biomimetic membranes for structure-function studies and biosensing applications. A better understanding of how the phase properties of supported membranes compare with those of the classical, free-floating lipid vesicles is however needed. The gel-to-fluid phase transition is one of the main physical properties that characterize aqueous dispersions of phospholipids. Variable temperature atomic force microscopy has therefore been used to investigate solid-liquid phase transitions in supported bilayers prepared by the Langmuir-Blodgett technique. We have investigated the melting behavior of fully-hydrated bilayers formed from dialkylphosphatidylcholines of different chainlength, and show that unlike their vesicle counterparts, the two leaflets of supported membranes can exhibit distinct melting.

COLL 77 In situ studies of amphiliphilic peptides at the solid-liquid interface using sum frequency generation vibrational spectroscopy, atomic force microscopy, and a quartz crystal microbalance

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The adsorption properties of model peptides have been studied with Sum Frequency Generation Vibrational Spectroscopy (SFG-VS), Atomic Force Microscopy (AFM), and Quartz Crystal Microbalance (QCM) at the hydrophobic (polystyrene) and hydrophilic (silica) solid-liquid interface. The peptides are isosequential in the hydrophobic (X) and hydrophilic (Y) residues: Ac-XYYXXYXXYYXXYX-NH2 where X and Y correspond to Leucine (L) and Lysine (K); Alanine (A) and Arginine (R); and Phenylalanine (F) and Arginine (R). These LK, AR, and FR peptides exhibit different adsorption

behavior from each other and on the different surfaces. SFG spectra show that on polystyrene, all peptides show strong C-H resonances which are characteristic of the modes of their hydrophobic side-chains. However, on silica, N-H modes are observed for LK peptide whereas adsorption of the AR and FR peptides show no distinct peptide modes but drastically change the surface water structure following adsorption. AFM and QCM results will also be discussed.

COLL 78 Influence of dihydrocholesterol on the vesicle bilayers of phosphatidyl cholines

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Vesicles of lipids such as phosphatidylcholines are excellent models to discern the structure and dynamics of cell membranes. The bilayer region of the vesicles is complex with lateral and transverse diffusion and flipping of molecules between inner and outer leaflets contributing to its dynamic nature. Cholesterol and dihyrdrocholesterol have been postulated to provide stability to the bilayer by embedding themselves in the hydrophobic region leading to a new phase termed the ordered liquid phase. We have investigated the dynamics of the bilayer region of dimyristoyl phosphatidylcholine (DMPC) at various concentrations (0-50 mole percent) of dihyrdrocholesterol employing a very small concentration of lipids with a fluorescent dye molecule on the polar head (NBD-PE) or hydrophobic tail NBD-PC) as the probe molecules for the bilayer region. The bilayer dynamics was investigated by quenching the fluorescence of the dye with dithionite in the temperature range 5 – 40 oC. At low dihyrdrocholesterol concentrations (up to 30 mole percent) the rate constant (k) for quenching undergoes an anomalous change at the phase transition temperature of 23 oC but ln k has a linear dependence on 1/T (T = temperature in K) below and above the phase transition temperature. At high dihyrdrocholesterol concentrations the anomalous rate constant change at the phase transition temperature vanishes with a linear dependence of ln k on 1/t over the entire temperature range. The enthalpies and entropies of activation determined from these studies indicate that high concentrations of dihyrdrocholesterol introduce a high degree of order to the bilayer region analogous to vesicles of natural lipids such as EggPC. Significant results of these studies will be presented.

COLL 79 Influence of head and tail labeled lipids on the membrane structure of phosphatidylcholines

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The bilayer regions of vesicles made of synthetic phosphatidylcholine lipids are excellent models for discerning membrane dynamics and its influence on transport through a cell membrane. The membrane dynamics is influenced by inherent inhomegenity and order or disorder (defects) introduced by the presence of other molecules in the bilayer region. We have investigated the influence of concentrations of lipids with a very small amount of fluorescent dye on the head (NBD-PE) or tail (NBD-PC) groups on membrane structure and dynamics by studying the fluorescence intensity and rate of fluorescence quenching by the addition of dithionite ion. These studies have been conducted (i) with a homologous series of phosphatidlycholines with carbon chain lengths of 12-18, (ii) below, at, and above their phase transition temperatures, and (iii) over a wide temperature range for dimyristoyl phosphatidylcholine (DMPC) (phase transition temperature = 23 oC). The quenching kinetics and the enthalpies and entropies of activation for quenching exhibit a strong dependence on the location of the dye molecule, namely, lipid head vs. tail. The important conclusion from these studies are (i) the tail labeled lipid NBD-PC introduces a higher level of disorder in the bilayer than the head labeled lipid NBD-PE and (ii) the fluorescence quenching has an negative entropy of activation implying a restoration of order in the bilayer accompanying quenching. The important results of these studies will be presented.

COLL 80 Investigation of membrane dynamics of vesicles of phosphatidylcholines

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Lipid membranes play a critical role in the selective transport of ions and molecules in and out of cells. Characterization of the bilayer structure of cell membranes has become very important for the emerging fields of lipidomics and bionanotechnology. The lipid bilayer is a complex entity governed by ensemble behavior of the self-assembled lipid molecules. Of particular importance is the role of transverse and lateral inhomegenity of the bilayer that influences membrane dynamics and facilitates the transport process. We have investigated the membrane dynamics of vesicles of phosphatidylcholines by incorporating a very small concentration of head (NBD-PE) and tail (NBD-PC) labeled dyes and quenching the fluorescence by the addition of dithionite ion. The kinetics of quenching have been conducted with: (i) a homologous series of synthetic phosphatidyl cholines with carbon chains lengths of 12-18 below, at, and above their phase transition temperatures, (ii) the vesicles of dimyristoyl phosphatidylcholine (DMPC) (phase transition temperature = 23 oC) and the natural systems EggPc and SoyPC, over a wide temperature range and (iii) the DMPC vesicles with dihydrocholesterol incorporated in the bilayer in the concentration range of 0-50% mole percent. The extent of fluorescence quenching and the enthalpies and entropies of activation provide valuable insights into membrane dynamics. Significant results of these studies will be discussed.

COLL 81 Towards the design of bioresponsive hydrogels

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We present a new class of bioresponsive hydrogels that enable label-free biosensing. The hydrogel is reversibly sensitive to a specific ligand, while its response is free from nonspecific binding interferences. To achieve these goals, we fabricated hydrogel microparticles (>1 micron in diameter) composed of poly(N-isopropylacrylamide-co-acrylic acid) (pNIPAm-co-AAc) via aqueous free-radical precipitation polymerization. To render the microgels antibody reactive, a portion of the AAc groups are used to couple an antigen (biotin, as H2N-Biotin) and aminobenzophenone (ABP) via EDC and DCC coupling, respectively. Functionalization by ABP allows for photo-tethering of anti-biotin. These functionalized microgels are then Coulombically assembled onto an aminopropyltrimethoxysilane (APTMS)-functionalized glass substrate to form supported microlenses. Bioresponsive microlenses are then prepared by exposure to a buffered solution of polyclonal anti-biotin, which binds to the microlenses via antibody:antigen interactions. Photoligation of the surface-tethered ABP to the antigen-bound antibody is accomplished via UV irradiation. The microlens focus was then reversibly modulated by displacement of the biotin:anti-biotin pair with free biocytin. Most importantly, the sensitivity of each microlens can be tuned by controlling the critical number of displacements required to cause microlens swelling. These results suggest that the microlens method can be an appropriate one for label-free biosensing of proteins or small molecules via displacement of tethered protein-ligand pairs.

COLL 82 Polymer nanostructure formation and polymerization kinetics in liquid crystals

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The ability to control nanostructure in materials has recently generated significant excitement over the past few years. While development of inorganic materials with specific structures on the nanometer size scale has been repeatedly demonstrated, similar structures in organic materials have been much more elusive. Promising routes to such materials will be discussed that utilize a

combination of photopolymerization and liquid crystals, both thermotropic and lyotropic, to allow templating for nanostructured organic polymers. While the molecules and phases in thermotropic and lyotropic liquid crystals are substantially different, the dynamics that govern control of the polymeric structure are remarkably similar and are strongly dependent on photopolymerization behavior. Furthermore, the polymer properties are remarkably dependent on the ultimate polymer nanostructure. This talk will focus on the factors that drive the unique polymerization kinetics in these systems, and the relationship between the kinetics and polymer nanostructure evolution.

COLL 83 Formation of polyelectrolyte/surfactant aggregates through polymerization of wormlike micelles

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Upon polymerization, wormlike micelles of (CXH2X+1)trimethylammonium 4-vinylbenzoate (CXTVB) form polymer/surfactant aggregates with properties that are unique for solubilized polyelectrolytes. These properties include high aqueous solubility, temperature stability, and pH-sensitive rheology. In addition, the CXTVB system represents the first use of a rod-like micelle template as the starting point for monomer ordering in a polymerization. These aggregates each contain, on average, one immobilized polymer chain. This polymer makes the aggregate dimensions insensitive to concentration and other solution conditions. The radial dimension of these rods is set solely by the surfactant tail length of the template (1.7, 2.0, or 2.4 nm). The length is independent of the initial micelle template length, and is controlled by the kinetics of the polymerization reaction. By controlling the rate of initiation, the lengths of these aggregates are varied between 90 and 500 nm. This use of elongated micellar structures offers a novel approach to the production of high aspect ratio, water-soluble amphiphilic nanorods.

COLL 84 Self-assembly of polymerizable cationic surfactants

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Two classes of surfactants cations containing polymerizable groups are investigated; dodecyldimethylammonioethylmethacrylate and vinyl-N-dodecylpyridinium salts. We will describe studies of the bulk and interfacial assembly of these polymerizable surfmers employing a combination of small-angle neutron scattering, neutron reflectometry and atomic force microscopy. Their self-assembly and their polymerization behaviour depend critically on the counterion, an effect that seems to have been overlooked in earlier studies. By ion exchange and electrolyte addition we will show how aggregate morphology and phase behaviour changes for acetate, chloride, bromide, salicylate and trifluoromethanesulfonate salts, allowing under some circumstances preservation of morphology post-polymerization. The behaviour of mixtures with conventional (non-polymerizable) surfactants will also be described.

COLL 85 Aqueous-core capsules via interfacial free-radical alternating copolymerization

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Aqueous-core capsules have wide-ranging applications in the high efficiency encapsulation and controlled delivery of drugs, dyes, enzymes, and many other substrates. Here, we produce liquid-core capsules with aqueous cores and uniform, controllably thick polymeric shells based on interfacial free-radical alternating copolymerization. Aqueous core capsules in the range of 0.25 µm to 10 µm diameter are prepared by interfacial polymerization of inverse emulsion drops with oil soluble maleate esters and water-soluble vinyl ethers. Confocal and transmission electron microscopy are

used to demonstrate a liquid/hollow-core structure and fluorescent dyes are used to measure capsule release characteristics.

COLL 86 Templating in micelles and vesicles

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Hydrotropes bind strongly to surfactant micelles, and can facilitate the formation of interesting microstructures such as elongated micelles and vesicles. Utilization of these microstructures as templates is attractive for the synthesis of organic materials with well-defined morphologies and length scales. Polymerization can create robust replicas of these microstructures with increased mechanical strength and stability under a variety of conditions. Here the formation and templating of vesicles and worm-like micelles comprised of polymerizable surfactants and hydrotropes will be described. The use of polymerizable species allows for the production of stable structures directly from the template. A variety of measurements allowed us to quantify and confirm that the vesicle dimensions were essentially unchanged during polymerization. Conversely, the micelles elongated during the course of the reaction, although their cross-sectional radius remained unchanged. This elongation likely results from the interplay of the micelle dynamics and the degree of reactivity of the polymerizable group.

COLL 87 From photo-reactive nanoparticles to photo-cleavable microcapsules

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We show how photocrosslinking of hydrophobic photoreactive polyorganosiloxane nanoparticles within the micrometer-sized thin oil shell of water-oil-water emulsion droplets forms a new species of optically addressable microcontainers. The inner water droplet of the double emulsions may contain drugs, dye molecules or other water-soluble components, leading to filled containers. Thickness, mechanical stability and light resistance of the container walls can be controlled in a simple way by the amount and adjustable photoreactivity of the nanoparticles. To obtain better defined microcapsules in comparison to those prepared by standard batch emulsification, we also have employed microfluidic devices for the formation of monodisperse water-oil-water emulsion microdroplets. Importantly, the chemical bonds between the nanoparticles constituting the microcapsule shell can be cleaved photochemically by irradiation with UV light. This optically controlled destruction of our microcontainers opens up a pathway to controlled release of the enclosed components, as will be illustrated by the example of enclosed cyclodextrin molecules.

COLL 88 Photolyzable surfactants

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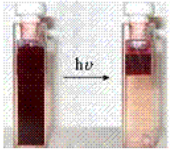
Photo-destructible surfactants such as C6PAS (sodium 4-hexylphenylazosulfonate) offer interesting opportunities for efficient and irreversible, light-triggered transformations in adsorption and aggregation. Dramatic changes in stability can occur by photolyzing the hydrophilic surfactant into insoluble hydrophobic photoproducts (hexylbenzene and 4-hexylphenol). For example vesicles and microemulsion droplets containing C6PAS can be broken down by UV light. Photo-induced phase separation of micelles and emulsions has been demonstrated when C6PAS is mixed with an inert non-ionic surfactant in the presence of salting-out electrolyte. The initial micellar systems can disperse an insoluble additive marker dye (shown), which may be spatially segregated from the aqueous environment by the action of UV light. These new concepts may find applications in light directed delivery and deposition of hydrophobic and/or hydrophilic constituents of multi-component functional systems.



COLL 89 Utilization of thermally cleavable surfactants based on furan and maleimide Diels-Alder adducts as removable templates

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Surfactants are molecules that have the ability to self-assemble into a variety of supramolecular structures that are effective templates used in the synthesis of a diverse range of materials. Efficient surfactant removal becomes increasingly significant in the synthesis of extended mesoporous and nanosized structures such as semiconductor nanocrystals, ceramics, polymers, and polymer-ceramic composites. Incorporation of a cleavable linkage into surfactant molecules could potentially solve this problem by allowing the removal of the surfactant templates through the thermally triggered formation of small, easily removed fragments. We have utilized our expertise in thermally cleavable materials to synthesize a new class of cleavable surfactants based on the Diels-Alder reaction that degrade after exposure to mildly elevated temperatures (< 95 degrees C). We present here the results obtained by utilizing these cleavable surfactants as templates in the development of polymeric monoliths and mesoporous silicates, and compare these materials to those produced by analogous surfactants.

COLL 90 Nanofabrication in data storage

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The rapid growth in density in data storage has pushed the industry well into the nanofabrication regime. Over the end of the 1990's, the storage density grew at an annual rate of 100%. Due to large technological challenges the growth rate has since slowed to less than 50%. Still, today, thin film heads with 100nm critical dimensions are being routinely fabricated in manufacturing. The physical trackwidths of read head sensors are shrinking rapidly. As trackwidths and bit sizes continue to shrink, we are rapidly approaching a point where the bits in current conventional disk media will no longer be thermally stable. A leading solution to the superparamagnetic effect is patterning the media. At 300 Gb/in^2, the center to center pitch of the bits will be under 50 nm. 1 Tb/in^2 will require a bit pitch of 25 nm. The patterning of the disks must also be accomplished in a high throughput manner. The lithographic requirements for data storage are rapidly surpassing the tooling and processes available from the semiconductor industry. In addition, the magnetic storage materials are difficult to pattern and unique to the data storage industry. This presentation will focus on the development of nanolithography and nanofabrication for future data storage manufacturing.

COLL 91 Spatial resolution limits of electron beam nanopatterning

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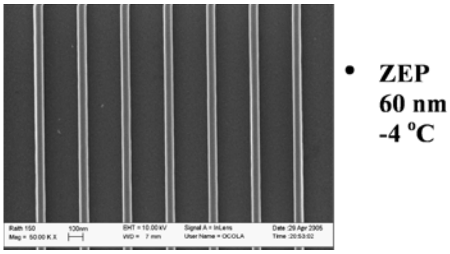
Electron beam lithography has represented the most effective way to pattern materials at the nanoscale for almost four decades. The success of e-beam lithography depends on multiple factors such as electron optics, the interaction between the beam of electrons and the pattern material (resist), and the interaction between the developer and the exposed resist. We will discuss the spatial resolution achievable with electron beam lithography by using a well established Monte Carlo model for electron beam simulations (LESiS) and a novel image formation model (soluble site density model) used successfully for chemically amplified resists. The soluble site density model can be adapted for describing the image formation in any photoresist. This includes chemically amplified resists and non chemically amplified resists, such as PMMA. In the case of PMMA this is done by modifying the Greeneich formula for PMMA dissolution as a function of density of scissions instead of absorbed dose density. PMMA is the resist that historically has exhibited the highest patterning resolution, and we will discuss why this is possible. We will address other factors that limit the spatial resolution of ebeam nanopatterning in resists, such as exposure statistics, the development process, and the drying process.

Figure 1. Example of cold developed (at -4°C) resist exposed with electron beam lithography. Grating of isolated 60 nm lines in 200 nm thick ZEP520 resist showing less than 5 nm line edge roughness. The open areas were exposed using a 30 KV ebeam tool.



COLL 92 Nanoscale electric lithography (NEL)

Wenjiang Shen, Haixiong Ge, Justin Chang, Yong Sik Ahn, Thomas Hahn, and **Yong Chen**, Department of Mechanical and Aerospace Engineering, University of California, Los Angeles, 48-121 Engineering IV, 420 Westwood Plaza, Los Angeles, CA 90095-1597, yongchen@seas.ucla.edu

A new nanoscale manufacturing technique — nanoscale electric lithography (NEL) is proposed for the fabrication of nanoscale patterns on resists by using an electric mask. The NEL process is simple and straightforward: A layer of resist is coated onto a substrate-supported bottom electrode, and then a mask with conductive metal patterns that are separated by insulating materials is pressed down toward a resist layer. An electric field is applied between the top and bottom electrodes. The resists residing between the electrodes will be configured (or "exposed"). After the top mask has been removed, the resist in the exposed areas can be eliminated selectively from the bottom electrode with solvents. Since electrochemical polymerization ("exposure") happens only on the substrate surface, the mask surface is left intact and the mask can be easily separated from the substrate without contamination. Nanoscale patterns transferred from the mask to a resist layer have been demonstrated. By selectively applying voltages to different conductive patterns on a mask, NEL can also be used to generate on-demand patterns. Moreover, by controlling the amount of monomers polymerized during the electrochemical process via changes in the electrochemical voltage, current,

and total charge flowing through individual conductive patterns, we can make 3D patterns with different heights on the substrate.

COLL 93 Nanoimprint lithography: Capabilities, applications, and challenges

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After almost a decade of research and improvement, nanoimprint lithography (NIL) is beginning to catch eyes of the semiconductor industry as a candidate for next generation lithography (NGL) technology. The powerful combination of its high-resolution, high-throughput, and low cost enables rapid extension into many emerging applications in the fields of MEMS, bio-nanotechnology, photonics, massive storage, etc. This talk reviews the recent development of nanoimprint lithography, presents its new capabilities and applications, and then discusses the key issues and challenges such as resolution limits, three-dimensional patterning, template technologies, new materials, and characterization of template/pattern transfer. Emerging applications in biochemical patterning, 3D bio-MEMS, tissue engineering, organic LEDs, and photonic crystals will also be presented.

COLL 94 Lithographic performance of resists based on polymers having a photoacid generator (PAG) in the backbone for EUV and 193 nm

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Polymer bound cationic type PAG resists, poly(HOST-co-EAMA-co-PAG1Tf) and poly(HOST-co-EAMA-co-PAG2Nf) have been synthesized and evaluated as potential components of EUV and 193 nm resist materials with enhanced lithographic properties such as photospeed and LER. These polymer bound cationic PAG resists exhibited faster photospeed and lower LER than the corresponding blend PAG resists, poly(HOST-co-EAMA) blend PAG3(Tf) and poly(HOST-co-EAMA) blend PAG4(Nf). These results imply that these novel resists have potential advantages over conventional resists and should be further explored for application in EUV as well as 193 nm lithography. Furthermore, use of different counter anions such as triflate and nonaflate influenced the lithographic performance. Sub-100nm features were obtained with enhanced lithographic performance using EUV as well as 193 nm exposure. More recent results incorporating anionic PAGs within various resists will also be presented.

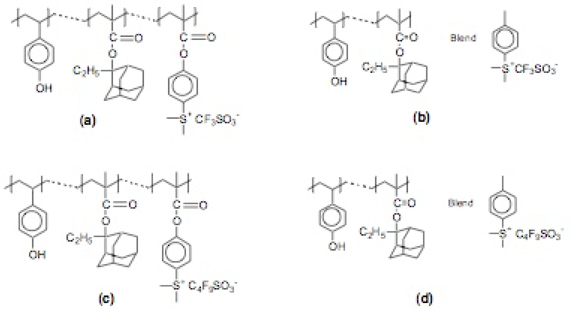

FIG. 1. Chemical structures of polymer bound PAG and blend PAG resists : a) poly(HOST-co-EAMA-PAG1) ; b) poly(HOST-co-EAMA)blend PAG3; c)Poly(HOST-co-EAMA-PAG2) and d) poly(HOST-co-EAMA)blend PAG4.

COLL 95 Achieving high resolution patterning using molecular glass photoresists

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Molecular glasses are a family of glass forming organic molecules that only recently have been investigated as high-resolution photoresists. One of the challenges of working with today's polymeric photoresists is the fact that even the small size of these polymers approaches that of the target features of next generation lithography. By using molecular glasses, in effect the pixel size of the resist is reduced to ~1 nm. This presentation describes recent developments in the synthesis and lithographic processing of these new materials. Two families of materials will be described: (i) molecular glasses capable of development in aqueous systems and (ii) molecular glasses that can be developed in environmentally friendly supercritical CO2. Both groups have been shown to be capable of forming images smaller than 50 nm using both e-beam and deep UV lithography.

COLL 96 Fleximags: New tools for micromechanical studies of biomolecular assemblies

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Magnetic colloidal particles can be readily assembled into one-dimensional structures by field induced dipole-dipole interactions. When interacting polymers are adsorbed on the colloid surfaces, the filaments can be made into permanent flexible filaments, or "fleximags". Their bending properties is then determined by the mechanical properties of the linking polymers. We use a specific dynamical behavior of fleximags to measure their bending stiffness. Biomolecular assemblies extracted from cells and functionalized to interact specifically to the colloids can also act as linkers. We are using this new tool to probe the association of centrin molecules, these proteins being suspected to play an important role in mechanotransduction within cells.

COLL 97 nSelf-assembly of protein Nanocapsules

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The precision of natural protein nanostructures is remarkable, and they can be used as scaffolds upon which to build new functionalities. We are investigating the use of genetically-engineered protein assemblies as carriers for pharmaceutically-active molecules. Our model system is the E2 component of pyruvate dehydrogenase, a protein complex that naturally self-assembles to form a 25-nm hollow spherical complex in which guest molecules potentially can be encapsulated. Examination of the self-assembly characteristics through site-directed mutagenesis has revealed the system's robustness with respect to changes in the internal cavity. This property is important for establishing the scaffold's potential as a molecular carrier in targeted drug delivery.

COLL 98 Triblock copolymers as nanoparticulate iron targeted delivery vehicles for source-zone remediation of contaminated aquifers

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Subsurface residuals of dense non-aqueous phase liquids (DNAPL) trapped in the microporous soil are a persistent source of mobile groundwater contamination. Conventional remediation methods only address the dissolved contaminant plumes, not the source, and are inefficient. We have proposed a “targeted delivery” approach to remediate trichloroethylene-contaminated groundwater, inspired by analogy to targeted drug delivery technologies. The remediation agents are nanoparticles with reactive, zero valent iron cores protected by iron oxide shells. These reduce TCE to non-toxic compounds. The targeting is based on nanoparticle surface modification with environmentally responsive ABC triblock copolymers prepared by atom transfer radical polymerization. The poly(methacrylic acid) A block anchors the polymer to the nanoparticle surface. The poly(styrene sulfonate) C block disperse the nanoparticles in water and repels soil mineral and humic substances. The hydrophobic poly(methyl or butyl methacrylate) B block swells in contact with TCE and anchors the particles at the TCE/water interface.

COLL 99 High throughput approaches to analysis of complex mixtures

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Most materials are complex mixtures of components and knowledgeable blending to achieve useful properties is the art of formulation. Classes of formulated products include plastics, paint and coatings, paper, concrete, glass, composites, cosmetics, personal care products, food, pharmaceuticals, cleaning products, lubricants, and adhesives. While each of these industries uses similar formulation techniques, the methods are often developed in isolation and furthermore they are often based on “trial-and-error” approaches. The emergence of high throughput and combinatorial approaches offers the potential to unify methodologies and concepts that are applicable across many industries, and to advance the fundamental understanding of formulation science. Examples will be presented for screening the effects of co-monomer composition and reaction time on the structure, properties, and biological responses of model blends; methods for high throughput analysis of block copolymer solution structures; and techniques for determination of stabilization in multiphase solution mixtures.

COLL 100 Role of oscillatory structural forces in sedimentation of a colloidal suspension

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Recent research conducted in our laboratory using thin colloidal films has revealed that the suspensions of micrometer-sized particles (or emulsions or foam bubbles) can be stabilized through the interactions of nanometer-sized particles, surfactant micelles, or globular proteins due to the ordering of small particles or micelles around larger ones. This breakthrough provides the motivation to establish the role of both the structural force arising from the repulsive energy barrier caused by particle/micelle microstructuring, and the attractive depletion force caused by the excluded volume effect in dispersion stability. Building on this discovery, we investigate the effects of depletion attraction and structural barrier both experimentally using a nondestructive Kossel diffraction technique and theoretically using rigorous statistical mechanical theories. Sedimentation experiments of nearly hard- sphere fine-particle suspensions was investigated. Particle concentration profiles and changes in sedimentation rates were monitored experimentally. These data were then compared with the theoretical results based on Monte Carlo and stochastical molecular dynamics simulations. The many-body collective effect resulting in particle crystallization is highlighted.

COLL 101 Polyelectrolyte/surfactant aggregates. Influence of the polymer backbone rigidity

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Studies of aqueous solutions of polyelectrolytes and surfactants of opposite charges will be presented. Various techniques have been used : specific electrodes, scattering of light, X-ray and neutrons, electrophoretic mobility. We will show results obtained with cationic surfactants and anionic polyelectrolytes of different backbone rigidity, including DNA. In some cases, we find well defined aggregates, with a size controlled by the surfactant concentration. These aggregates possess an internal structure, similar to that of the liquid crystalline phases obtained in the precipitated phases obtained at higher surfactant concentrations.

COLL 102 Neutron studies of multicomponent interfacial layers

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Neutron reflection can provide information about both the composition and structure of layers at a variety of interfaces. Selective deuteration of solvent or other components can be used to identify the average location of particular species. Recent work on adsorption of biopolymers to solid/liquid interfaces will be presented to illustrate the particular advantages.

COLL 103 Molecular level studies of buried interfaces involving polymers and biological molecules using SFG

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Sum frequency generation (SFG) vibrational spectroscopy has been applied to investigate molecular structures of buried interfaces such as polymer/water and polymer/protein solution interfaces. Various polymers such as polymethacrylates, polyurethanes, and silicones have been used in the study. It was found that they can have very different surface restructuring behaviors in water. SFG revealed such behaviors qualitatively as well as quantitatively. Interfacial interactions between these polymer materials and biological molecules such as proteins and peptides have been studied. SFG amide I signals from various secondary structural motifs such as alpha-helices and beta-sheets have been analyzed in detail using irreducible representations and projection operators. SFG measurements have been correlated to results obtained from molecular dynamics simulations. Time-dependent structural changes of proteins after adsorption to polymer surfaces have been monitored using SFG. This research demonstrates that SFG is a powerful technique to elucidate molecular structures of polymers and biomolecules at interfaces.

COLL 104 Planar lipid bilayer fabrication by solvent extraction in a microfluidic channel

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Membrane channel proteins (MCPs) have received much recent attention as tools for single-molecule sensing elements and as targets for drug discovery and drug safety testing. A popular method for studying electrical currents through MCPs requires the fabrication of planar lipid bilayers; unfortunately, existing techniques for lipid bilayer fabrication require direct attention from an experienced operator. They are therefore not amenable to automation or high-throughput formats. We have developed a novel technique for forming lipid bilayer membranes in a poly(dimethylsiloxane) microfluidic channel by extracting the solvent from a droplet of lipid solution. The presence of a molecular bilayer and the insertion of single molecules of the pore protein alpha-hemolysin into such a bilayer has been confirmed by electrical measurements. This technique is

automatable and can be integrated into a larger microfluidic system to facilitate high-throughput in vitro screening of membrane channels or autonomous sensor devices.

COLL 105 Creating air-stable tethered lipid bilayers as cell membrane mimics

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Lipid bilayers on solid substrates have shown great promise as cell membrane mimics. Potential applications include drug discovery and biosensors. To date, the fragile nature of biomimetic lipid bilayers have precluded their incorporation into practical devices, such as biosensors, due to their lack of stability. In this paper, we report on tethered lipid bilayers (t-BLM) that were made stable against exposure to an air interface when dried for long-term storage. Upon rehydration the t-BLM regains nearly all of its functionality. We will discuss the role of drying process parameters, formulations and provide some mechanistic insights.

Our t-BLM is made of phytanyl lipids and is linked to a gold substrate via disulphide bonds. Moreover, the t-BLM possesses an ionic reservoir made of hydrophilic ester linkers suitable for the incorporation of membrane proteins, especially ion-channels. We characterize our lipid bilayers at different processing stages by electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), fluorescence microscopy, fluorescence recovery after photobleaching (FRAP), and the ability to incorporate membrane proteins, in our case the ion channel gramicidin-A. Bilayers stored wet lose physical integrity and functionality within a few weeks. EIS measurements indicate loss of electrical seal due to increased leakage conductance. Tapping AFM reveals lipid bilayer rearrangement leading to desorption and the appearance of bilayer-free defect patches. In contrast, rehydrated bilayers remain insulating even after prolonged dry storage. Further incorporation of gramicidin allows dimer formation and rise in conductance levels. FRAP studies show that fluidity (percent recovery) and mobility (in-plane diffusion constant) of rehydrated bilayers remain comparable to the fresh, never dried, state.

This approach enables long-term storage in the dry state, while taking advantage of the self-assembly nature of lipids in their fluid, wet state for device manufacture.

COLL 106 Single channel activity from ion channels in engineered tethered bilayer membrane arrays

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The demand for rapid in situ detection of chemical and biological analytes at high sensitivity has increased interest in the development of biosensors. Engineered membrane bound ion channels are promising biological receptors since they would allow for the stochastic detection of analytes at high sensitivity. For stochastic sensing it is necessary to be able to measure the ion currents associated with single ion channel opening and closing events. By interfacing the synthetic ion channel M2δ based on the channel-lining domain of the nicotinic acetylcholine receptor (nAChR) from *Torpedo californica* to a microelectrode array device we have made the first measurement of single channel activity from a tethered bilayer system. The limited size of the gold sense pad surface, 100x100 μm^2, and the electrical stability of the overlying lipid bilayer membrane make each individual pixel of the microelectrode array device sensitive enough to measure single ion channel currents in the picoampere range.

COLL 107 DNA adsorption and compaction at interfaces

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The behavior of DNA at different types of interfaces and how the formed structures DNA at an interface could be affected by cationic surfactant will be discussed. This includes DNA interaction with macroscopic flat surfaces, with nano-particles and lipid/surfactant monolayers studied by ellipsometry, light scattering, neutron scattering and reflectometry, and surface film balance. Adsorption of DNA-cationic surfactant complexes is determined by a delicate balance of DNA-surface, cationic surfactant-surface, and cationic surfactant-DNA interactions. Particular attention will be paid to how the type of cationic surfactant and DNA (single or double stranded and length) affects the compaction/decompaction of DNA and how this can be used to control the compaction of DNA.

COLL 108 Label-free biosensor based on ultrathin film of biotin-functionalized poly(3-aminobenzoic acid)

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An ultrathin film of self-doped polyanline derivative, poly(3-aminobenzoic acid) (PABA), was prepared for biosensing applications. An aniline-terminated thiol was immobilized on a gold substrate by self-assembly in order to provide anchor groups for polymerization of 3-aminobenzoic acid. A homogeneous and ultrathin (2-4 nm) film of PABA was obtained by electrodeposition on aniline-terminated thiol monolayer in 0.5 M H_2SO_4. The resulting PABA films showed good electroactivity in neutral aqueous solution (pH = 7.4). Carboxylic acid groups on the film were treated with N-hydroxysuccinimde then reacted with biotin ethylenediamine. The binding events of different proteins (e.g. avidin, streptavidin) to biotin immobilized PABA films were investigated using electrochemistry and surface plasmon spectroscopy. A 0.5 cm^2 biotin-functionalized PABA electrode showed clear decrease of electrochemical activity upon the addition of as low as $6x10^{-14}$ mole (femto mole) of avidin in PBS solution. The electropolymerized PABA ultrathin film is a promising platform for label-free biosensors.

COLL 109 Naturally engineered glycolipid biosurfactants leading to distinctive self-assembled structures

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Self-assembling properties of “natural” glycolipid biosurfactants, Mannosyl-erythritol lipid A, B (MEL-A, MEL-B), which are abundantly produced from vegetable oils by yeast strains, were investigated using the fluorescence probe method, dynamic light scattering (DLS), freeze-fracture transmission electron microscopy (FF-TEM), synchrotron small/wide angle X-ray scattering (SAXS/WAXS) and so forth. Both MEL-A and MEL-B exhibit an excellent self-assembling property at extremely low concentrations; MEL-A, which has an acetyl group at the C-4' position on the headgroup, gives two critical aggregation concentrations (CACs), whereas MEL-B, which has a hydroxyl group at the C-4' position, gives only one CAC. They self-assemble into large unilamellar vesicles (LUV) just above their critical aggregation concentration (CAC_I). Moreover, the self-assembled structure of MEL-A above CAC_{II} is found to drastically change into sponge structures (L_3) composed of a network of randomly connected bilayers. The unique and complex molecular structures would provide the sophisticated self-assembling properties of the glycolipid biosurfactants.

COLL 110 Dynamics of surface catalyzed reactions. The roles of surface defects, surface diffusion and hot electrons

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The pioneering work of Steve Bernasek of studies of H2D2 texchange on platinum single crystal surfaces has set the tone of surface reaction dynamics studies for many years. The important roles surface defects, steps and kinks play in bond activation has been uncovered early in the development of molecular surface science through studies of C-H, C-C and and CO bond activation. High pressure scanning tunneling microscopy permitted us to identify the importance of surface mobility of adsorbates during the catalytic reactions. Poisoning of the surface by an adsorbed molecule stops the mobility and stops the catalytic turnover. The detection of hot electrons at oxide-metal interfaces during exothermic catalytic reactions allowed monitoring of continuous flow of hot electron currents at the oxide-metal interface that act as Schottky barrier. It appears that hot electron generation that have about 10 nm mean free path and enough energy, 1-3 eV, to overcome a large Schottky barrier is an important part of exothermic catalytic reactions. This brings into focus the importance of oxide metal interfaces during catalysis that was already detected and identified by Schwab and others in the early 1960's. Adsorbate-induced restructuring of metal surfaces that become dominant at low coordination sites also point to the importance of atomic and molecular motion at surfaces during catalytic turnover.

COLL 111 Chemical dynamics at metal surfaces

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Conventional molecular dynamics simulations are inadequate to describe chemical processes at metal surfaces because electron-hole pair excitations contribute to or even dominate energy transfer; i.e., the Born-Oppenheimer approximation is invalid. This paper will describe recent efforts to incorporate electronic transitions self-consistently in an otherwise classical mechanical molecular dynamics framework. The non-adiabatic couplings responsible for electron-hole-pair transitions are recast in the form of frictions and fluctuating forces. The frictions and fluctuating forces are computed ab initio using plane-wave pseudopotential methods. Application of the method to elucidate the roles of electronic vs. phonon dissipation on vibrational lifetimes, inelastic scattering, and sticking will be presented, with comparisons to experiment. In addition, implications to “hot-electron” induced desorption and to single molecule vibrational spectroscopy in the scanning tunneling microscope will be described.

COLL 112 First principles study of nanoscale catalysis

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This talk will present an overview of our first principles study of catalytic behavior of nanoscale systems. These include interaction of CO with iron surface for CO oxidation, vacancy mediated CO oxidation on TiO_2 surface, and NO reduction on small Pd clusters. Combining our first principles study with experimental data we obtain an atomic level understanding of structure, reaction mechanism, role of interface and vacancy in these systems. Finally, we will present our recent first principles study of interaction of hydrogen molecule on metal coated nano-peapod structures which exhibit high wt% suggesting potential applications of peapod structures for hydrogen storage.

* The work is done in collaboration with Professors S. L. Bernasek, M. Nooijen, A. Selloni (Princeton) and P. Jena (VCU)

COLL 113 Closing the nonequilibrium gap between surface science, catalysis, and electronic structure theory

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Progress towards achieving a unified kinetic picture of surface reactions has been uneven when nonequilibrium surface science and thermal equilibrium catalysis experiments have been compared and contrasted with electronic structure theory (EST) calculations of transition state characteristics. A simple microcanonical unimolecular rate theory (MURT) model of gas-surface reactivity has been able to largely close this “nonequilibrium gap” for several activated dissociative chemisorption reactions [e.g., CH4 on Ni(100), Pt(111), and Ir(111); SiH4 on Si(100); H2 on Cu(111)]. The MURT's ability to quantitatively predict and directly compare the results of disparate equilibrium and nonequilibrium experiments to one another and to the calculations of EST will be shown to open up some useful new opportunities to rigorously test and refine our understanding of reactive transition states and kinetics at surfaces.

COLL 114 Internal energy of $CO_{2(g)}$ formed from the catalytic oxidation of methanol on a polycrystalline platinum surface

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The chemical dynamics of methanol oxidation on a polycrystalline platinum surface was investigated using infrared absorption spectroscopy with a tunable diode laser to measure the ro-vibrational state distribution of the nascent carbon dioxide. These measurements were made for a number of oxygen to methanol ratios and surface temperatures, and found that the asymmetric stretch of the $CO_{2(g)}$ produced is hotter than its bending and symmetric stretching modes. Furthermore, the temperature of the asymmetric stretch increases with the surface temperature while the bending and symmetric stretch modes do not. The amount of energy in the vibrational modes of $CO_{2(g)}$ produced upon methanol oxidation is less than that found for the oxidation of $CO_{(g)}$ by either $O_{2(g)}$ or $NO_{(g)}$ and follows a different surface temperature and reactant ratio dependence. This suggests that the CO2(g) formed from methanol oxidation is generated by a different reaction pathway than $CO_{2(g)}$ from $CO_{(g)}$ oxidation.

COLL 115 Carbon-induced corrosive reactivity of metal surfaces

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When carbon is transferred onto metal/alloy surfaces from carbon-supersaturated gaseous environments (CO+H2, for instance), several steps occur in sequence to trigger the ultimate degradation of the metal into a powder or dust. This form of "metal dusting corrosion" typically occurs in the temperature range, 450-850 C, the actual sequence of events depending upon the specific metal or alloy concerned. For example, in the case of Fe, the reaction steps include the initial surface transfer of carbon from the gaseous environment, followed by the formation of a metastable surface reaction product, Fe3C. The catalytic deposition of graphite that subsequently occurs on the Fe3C surface destabilizes the latter, leading to the creation of metal or dust. Slightly different mechanisms operate on other metals such as Ni or Co and high chromium Ni-base and Fe-base alloys. The detailed mechanistic picture of this type of surface degradation is presented. Two key approaches to control degradation are outlined: one deals with the suppression of the carbon transfer reaction while the other deals with the insitu formation of inorganic compound layers to resist inward carbon diffusion.

COLL 116 Surface vibrational spectroscopy of benzene hydrogenation on Pt(111): Pressure and temperature effects

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Hydrogenation of benzene on the Pt(111) crystal surface was studied using sum frequency generation (SFG) vibrational spectroscopy and kinetic measurements over a range of pressures (10^{-8}-15 Torr) and temperatures (300-440 K). SFG is a surface specific technique that directly probes the surface adsorbates without signal contribution from background gases. The vibrational spectra revealed both chemisorbed and physisorbed benzene co-adsorbed under high pressures at room temperature. This result differs from the previous ultra-high vacuum studies, which noted only one benzene adsorbate. Evacuation of the reactant gas after heating to 440 K results in an adsorbed hydrogenated benzene species, which is inline with previous infrared and DFT studies. The addition of 50 Torr of H_2 at 300 K after evacuation resulted in the formation of π-allyl c-C_6H_9. Below 370 K kinetic studies reveal only the formation of cyclohexane. Increasing the temperature above 370 K drastically enhances the production of cyclohexene as well cyclohexane.

COLL 117 Self assembly and dynamics of protein adsorption to cell adhesions

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Focal adhesions are cellular junctions, composed of proteins adsorbed from the cytoplasm, that connect cells to surfaces or to each other. They are important for tissue formation, wound healing and cancer. Experiments show that the growth of these domains of adsorbing and self-assembling proteins is anisotropic and occurs in the direction of the applied force. This is in contrast to the isotropic growth of self-assembled domains of surfactants, proteins or lipids adsorbed to interfaces. We present a model for this adsorption that couples the mechanical forces to the non-linear adsorption dynamics. Our results show that the relative motion of the front and back of the adsorption domain is asymmetric and in different ranges of forces, the adhesion shrinks or grows in the direction of the force, in qualitative agreement with observations. The growth of these domains can saturate at a size that is determined by the elastic deformation of the underlying substrate.

COLL 118 Polyelectrolyte-protein coacervates: Novel biomacromolecular fluids

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Coacervation with polyelectrolytes can immobilize proteins at high concentrations with no diminution of enzyme activity. Coacervates were prepared through pH-induced complexation of serum albumin with poly(dimethyldiallylammonium chloride). PDADMAC-BSA coacervation occurs over a wide range of conditions, yielding optically clear fluids containing above 200g/L protein, concentrations not normally homogeneously sustainable in solution but resembling those within cells. They exhibit large shear viscosities, but with protein diffusivities only an order of magnitude below those in dilute solution. We probed their microstructures using static light scattering, SANS, TIRF and Cryo-TEM, along with dynamic techniques, namely FRAP, DLS and rheology, the last two covering a range of polyelectrolyte MWs. These methods probe many length scales, providing a description of microscopic structure and dynamics. The results taken together indicate a solution-like state in which homogeneous fluid-like domains coexist with denser and more nearly charge-neutralized regions which inhibit local protein diffusion and confer transient network rheology.

COLL 119 Drug conjugate nanoparticle formation by Flash NanoPrecipitation

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Nanoparticle formulations of organic actives have been explored for various applications, including cosmetics, printing inks, and drug delivery. For instance, block copolymer nanoparticles offer unique advantages in cancer therapy by solubilizing hydrophobic drugs, reducing toxicity, and extending drug circulation times in vivo. The control of nanoparticle size and stability are required in these applications, and are greatly affected by the method used for nanoparticle production. Common techniques to form nanoparticles include slow anti-solvent addition and dialysis, and emulsification-based methods. However, most of these methods have serious limitations, including long processing times, process scale-up, low nanoparticle drug loading, and lack of control of nanoparticle size. A novel process, termed Flash NanoPrecipitation, for the production of nanoparticles was recently introduced. Flash NanoPrecipitation is an easily scalable technique that provides high solute loading, controlled size, and stable nanoparticles using amphiphilic diblock copolymer stabilization. The nanoparticle stability is dependent on the solute encapsulated. For example, controlled size β-carotene nanoparticles stabilized with a block copolymer of poly(ethylene glycol)-b- poly(styrene) with molecular weight of 3,000-b-1,000 g/mole respectively, were prepared by Flash NanoPrecipitation, and demonstrated stability for months. However, some solutes exhibiting hydrophobicities lower than β-carotene resulted in formulations that showed considerable recrystallization 20-30 minutes after nanoparticle formation. In order to stabilize the formulations and limit recrystallization, solutes were conjugated to a hydrophobic "anchor" consisting of a hydrophobic polymer or other organic component prior to mixing by Flash NanoPrecipitation. This resulted in nanoparticles with stable size, and no apparent aggregation or particle growth for over one week. The work presented here demonstrates the use of this approach through the conjugation of paclitaxel, an anti-cancer drug, to vitamin E succinate followed by formulation into controlled size nanoparticles via Flash NanoPrecipitation using methoxy poly (ethylene glycol)-b-poly (ε-caprolactone) block copolymer with molecular weight of 5,000-b-7,000 g/mole, respectively.

COLL 120 Evaporation-driven mixing and microseparations in droplets on a chip: Fundamentals and applications in materials synthesis and bioassays

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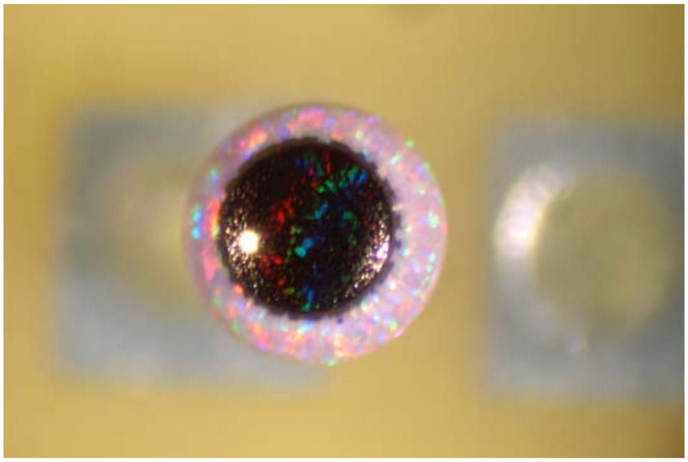
We will discuss the fundamentals and applications of processes taking place inside single microdroplets of water floating on the surface of dense fluorinated oil. The droplets are manipulated by electric fields created by addressable arrays of electrodes. Evaporation leads to rapid collection of the particles suspended in the droplets in their top region. Experimental results and numerical simulations show that the microseparation is driven by coupled mass and heat transfer processes. The flow pattern and temperature distribution inside evaporating droplets were simulated using finite element calculations. These phenomena could be used for on-chip "droplet engineering" processes where the droplets are used as sites for materials synthesis, encapsulation and microbioassays. We will demonstrate how the droplets can be used to assemble complex asymmetric particles, polymer microcapsules and inorganic shells. A new microbioassay technique based on particle agglutination inside droplets will be presented and analyzed.



COLL 121 Targeting and imaging with polymersomes

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We describe recent advances in the construction, functionalization, and packaging of polymersomes. We have successfully constructed polymersomes solely from a single biodegradable polyethylene oxide-polycaprolactone diblock copolymer. This technology offers an advantage over existing methods in which biodegradable polymers are blended with non-biodegradable polymers. Efforts to extend the palate of polymers to make polymersomes will be discussed. Further, we will describe wide ranging methods to functionalize polymersomes with peptides and antibodies for a spectrum of targeting applications, and how systematic construction of the polymersome interface allows us to design polymersomes for adhesion. Finally, we have now been able to encapsulate a spectrum of different agents within and on polymersomes, including porphyrins for optical imaging; tat-peptides for cell internalization; other imaging agents; and chemotherapeutic drugs. Thus, we are approaching the full potential of polymersomes as multi-functional carriers that can be targeted, imaged, and used to release therapeutics. Additional authors: I.-W. Chen, J. Lin, and D. Levine (Penn).

COLL 122 Mechanics of adhesion at the surface of polymer vesicles

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The adhesion and bending modulus of polybutadiene-poly(ethylene oxide) block copolymer vesicles made from a bidisperse mixture of polymers is measured using micropipette aspiration. A nonlinear relationship between the surface energy density and ligand concentration leads us to postulate a model for the vesicle surface that includes the extension of adhesive ligands from the surface brush of the vesicle. This contributes to the surface energy density by incorporating the amount of energy required to extend the polymer out of its equilibrium conformation prior to the breakage of surface bonds. The form of this component is developed from the the blob model of bidisperse polymer mixtures of Komura and Safran. The same model accurately reproduces the scaling of the vesicle bending modulus with polymer composition.

COLL 123 Nanoparticle construction by assembly of charged block copolymers or block copolypeptides

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By considering peptidic or charged, synthetic polymers in the materials self-assembly design process, one can take advantage of inherently biomolecular attributes; intramolecular folding events, secondary structure, and electrostatic interactions; in addition to more traditional self-assembling molecular attributes such as amphiphilicty, to define hierarchical material structure and consequent properties. First, diblock copolypeptides consisting of a hydrophilic, charged block and a hydrophobic block were designed to self-assemble due to their amphiphilic nature. The defined helical secondary structure of the leucine hydrophobic block forces these molecules to form a membraneous local nanostructure. However, diverse materials, ranging from rigid hydrogel, vesicle suspension, or hexagonal single crystal, can be formed depending on assembly pathway. 2) Synthetic triblock copolymers with charged corona blocks can be assembled in dilute solution with multivalent organic counterions to produce complex micelle structures such as toroids and discs. Nanostructure can be tuned with different concentrations or molecular volumes of organic counterion.

COLL 124 Self-assembly of block copolypeptides in solution

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This talk will describe the self-organization of poly(L-lysine)-b-polyglycine diblock and triblock copolypeptides in aqueous solution. A battery of methods including light scattering, conductivity, and microscopy are used to characterize the solution behavior. The results indicate that several different stimuli including pH, salt, and anions can be used to modulate the size and nature of the structures formed by these biomimetic macromolecules. These macromolecules form objects in solution whose size can be readily and reversibly modulated, and the occurrence of these size/structural transitions correlates with changes in conformation of the lysine block. The results of this work show that these previously unreported materials have unique properties of relevance to numerous applications including drug delivery, controlled released, encapsulation, and biomineralization/biomimetic syntheses of hard matter.

COLL 125 Protein adsorption at the oil/water interface by 3-D lattice dynamic monte carlo simulation

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Protein cooperative adsorption at the oil/water interface is simulated with a 3D lattice dynamic Monte Carlo algorithm. The interaction-parameter set is systematically explored and optimized for representing realistic behavior typical of many aqueous globular proteins (fast folding; nonaggregating in the bulk, but irreversibly adsorbing to and aggregating at the interface). A broad range of protein behavior emerges with small changes in the solvent interaction energies from nonaggregating, to reversibly aggregating, or to irreversibly aggregating into crystals or amyloid fibrils. A similar wide variety of fascinating behaviors occurs at the oil/water interface, ranging from nonadsorbing to reversibly to irreversibly adsorbing with different degrees of aggregation at the interface and penetration into one or both phases. The proposed energy scale is useful for quantifying the behavior of proteins in bulk solvents and at fluid/fluid interfaces as a function of protein size and composition.

COLL 126 Hydrophobic interactions relevant to biological assembly

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Water plays a critical role in mediating many complex self-assembly phenomena in aqueous solutions, including protein folding, micelle and membrane formation, and molecular recognition. Specifically through its structuring around various solution species, water can induce attractive or repulsive interactions between them, depending on their chemistry (hydrophobic vs hydrophilic), shape, and size. Molecular-level understanding of such solvation phenomena requires approaches that treat water explicitly and not simply as a dielectric continuum. We will present theoretical and simulation results on the lengthscale dependence of hydrophobic interactions, and highlight their relevance to condensed matter physics and to biological self-assembly. Knowledge of water-mediated interactions obtained over a broad thermodynamic space of temperature, pressure, and additive concentration can be integrated to understand a variety of biophysical phenomena. We will illustrate this point using an application to pressure denaturation of proteins.

COLL 127 Multiscale modeling of biomolecular systems

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We are studying lipid bilayers and their interaction with alcohols and sugars on various scales. Key experimental observable are deduced and their dependence on concentrations of the small molecule elucidated. For this problem we are using membrane models on three different scales ranging from an atomistic detailed model up to a two dimensional model with only one interaction center for each lipid. Intermediate models with one interaction center for groups of 4-6 heavy atoms are applied as well. We obtain that alcohols destabilize the membrane, this effect increases both with concentration as well as chain length. Some sugars, trehalose especially, on the other hand are stabilizing the bilayers. We conclude with an outlook to related problems like membrane-pathogen interaction and the phase behavior of biomembranes with and without the presence of small molecules.

COLL 128 Mixed methods for mixed membranes: Tail mutation moves for rapid equilibration in mixed-lipid bilayer simulations

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Because lipid lateral diffusion is slow compared to the duration of typical atomistic molecular dynamics (MD) simulations, a strong dependence on initial lateral distribution of different lipid types is a serious problem for simulations of lipid bilayers. In certain cases, this challenge can be overcome through kinetically unphysical, but thermodynamically rigorous, configuration-bias Monte Carlo (MC) “mutation” moves. A hybrid MD-MC approach has been implemented within the semi-grand ensemble for the study of mixtures of phosphatidylcholines with alkyl tails of different lengths, in particular the DLPC / DPPC mixture. Equilibrated mixed bilayers have been achieved through simulations with very reasonable computational cost. The structure of the DLPC / DPPC mixed bilayer will be presented, with particular attention to the possibility of intra- and trans-layer correlations in composition, along with results on partitioning of the two components across different micro-environments.

COLL 129 Hierarchical dynamical models of lipid bilayers interacting with surfaces

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The fabrication of membrane microarrays involves the binding of lipid bilayers to a solid substrate. We study the dynamical interactions between a lipid membrane and a glass substrate through a hierarchical multi-scale approach by linking the results of atomistic, coarse grained and continuum simulations of supported lipid bilayers. We use fully atomistic molecular dynamics to model the interactions of the bilayer with the substrate, thus extracting the energy of this interaction. The velocity correlations and fluctuation amplitudes from coarse grained simulations of this system are used to parameterize the continuum model, which is based on the fluctuation-dissipation approach. Our continuum model is used to study applications of SLBs through simulations on the order of hundreds of nanometers at time scales up to a microsecond, thus illustrating the power of the multi-scale approach. To our knowledge, this is the first numerical study of supported lipid bilayers involving this level of detail.

COLL 130 Multiscale modeling of platelet adhesion to surfaces under flow

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Platelets bound to the surface via the GPIbα-von Willebrand factor (vWF) molecular pair, exhibit rolling over the surface in the presence of shear flow, similar to leukocyte rolling. Platelets, however, are far from spherical in shape and appear as flattened ellipsoids. This difference in shape influences the cell's flow behavior near a solid boundary, ability to contact the surface, and the force mechanics of bond formation and breakage. We have developed a fully 3-D numerical adhesive dynamics model that incorporates both fluid mechanical solutions for platelet hydrodynamic flow near a planar surface and stochastic GPIbα-vWF binding kinetics. Platelets were found to exhibit three distinct flow regimes depending on their initial heights. Through our platelet tethering and rolling simulations we have characterized the nature of hydrodynamic force-loading on the platelet-surface bonds, resulting bond lifetimes, platelet pause times with average number of bonds formed, and surface distribution of bonds and bond forces.

COLL 131 Ion-specific effects on structure and thermodynamics of colloidal dispersions

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Phase behavior of colloidal and protein solutions is often controlled by the addition of simple electrolytes. In addition to nonspecific screening effects, salt ions interact with colloidal solutes through strongly specific dispersion forces. We estimate dispersion potentials between ionic species in saline colloidal solutions using McLahlan-Lifshitz theory and experimental or theoretical estimates for ion polarizabilities and ionization energies of major ions in water. Calculated potentials are employed in simulation and integral calculations of solution structure and thermodynamics. At realistic solution conditions, the influence of ion-polarizability is generally significant and often of comparable magnitude as coulombic interactions. Phase diagrams determined by perturbation theory reveal strong ion-specific effects consistent with experimental observations in globular protein solutions.

COLL 132 Connecting the wetting and rheological behaviors of PDMS-grafted nanospheres in PDMS melts

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Engineered nanocomposites are often formulated by grafting polymer brushes to the surfaces of colloids to optimally disperse them into viscous polymer matrices. In spite of the ubiquity of these filled materials, the essential mechanisms in producing an optimal dispersion have not been well quantified. To this end, rheological and light scattering measurements are made to connect the static wetting and dynamic flow properties of polydimethylsiloxane (PDMS)-grafted silica nanospheres in PDMS melts. By controlling the brush grafting density and the matrix chain length of these model systems, results indicate that the wetting and the flow behaviors can be quantifiably linked. Overall, these studies represent new ways of quantifying the factors that control the dispersion of polymer-grafted nanoparticles in viscous melts.

COLL 133 Another look at organic/metal interfaces based upon the topological features of the electron density

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In our previous study (P.M. Mitrasinovic, Can. J. Chem. vol. 81, pp. 542-554, 2003), the quantum theory of atoms in molecules (QTAIM) was fundamentally established as a valuable tool for the investigation of the nature of the interfacial interactions between organic molecules and metallic surfaces. The topological features of the electron density at the bond-critical point (BCP) provide quantitative information on the characteristics of a specific bond. In this work (P.M. Mitrasinovic, Technique-Tehnika vol. 60(4), pp. NM1-NM9, 2005), a general methodology for the determination of the nature of the interfacial interactions is proposed by investigating the changes of the organic/metal bond-critical parameters as consequences of both increasing the size and changing the shape of the metal clusters. In particular, the adsorption of acrylonitrile (AN) on the copper (100) surface is analyzed by considering model clusters (Cu_n, n = 9-14,16,18,20) for the actual surface. Statistical models with their goodness of the fitting of the data obtained by use of the topological analysis of the charge density at the AN/Cu_n (n = 9-14,16,18,20) BCPs are reported. In getting these results essentially associated with the electronic properties and reactivity of various copper clusters, no reference to orbitals has been invoked.

COLL 134 Interdiffusion and materials function in polyelectrolyte multilayer thin films

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The alternating adsorption of oppositely charged molecular species, known as the electrostatic layer-by-layer (LBL) process, is a simple and elegant method of constructing highly tailored ultrathin polymer and organic-inorganic composite thin films. We have utilized this method to develop a number of functional ultrathin film systems, including a range of electrochemical and power devices using multilayer assembly such as electrochromic displays, proton exchange membranes for fuel cells, and photovoltaic devices. These systems are also of interest in a number of biomaterials, including new drug delivery devices based on hydrolytic degradation. All of these systems rely on the ability to control the placement of different multiply charged components within specific regions of the film. Some of the polyion systems of interest in these applications, however, undergo some degree of interdiffusion during the assembly process, thus creating limitations in the function of electrochemical and biomedical devices. The nature of this interdiffusion, and means of controlling the interdiffusion process are discussed, as well as the final device applications of these systems.

Means of using the interdiffusion phenomenon in an advantageous manner to create ordered biomaterials assemblies will also be addressed.

COLL 135 Adsorption of atmospheric gases on hydrocarbon surfaces: Implications for solvent mediated interaction

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Despite its potential influence on the hydrophobic effect, and relevance in several other contexts, as diverse as decompression thickness and particle flotation, the presence of dissolved gases in ambient confined systems is often overlooked. Two recent experiments study the effect of deaeration on hydrophobic hydration and interaction. Dynamic surface-force apparatus measurements show a dramatic gas effect at long range (above 5 nm), but a minimal one at close range and in determining the adhesion force or interfacial energy (1). Neutron reflectivity measurements, on the other hand, reveal gas-specific depletion at hydrophobic/water interfaces (2), indicating change of interfacial tension with deaeration. To elucidate these experimental results, we performed open ensemble computer simulations of water-filled hydrocarbon-like confinements of planar geometry in equilibrium with ambient pressure N2 , CO2 (3), O2 or Ar. While we observe a considerable increase in the concentration of each of the gases in the immediate vicinity of confinement walls, the adsorption is still insufficient to produce surface-water depletion suggested by neutron reflectivity experiments or to rationalize the measured dependence of surface-forces on the presence of gas. These observations point to a possible role of non-equilibrium effects in these systems like the release of excess amounts of gases from surface materials, large sporadic density fluctuations, or the presence of nano-sized bubbles adhering to apolar walls. (Supported by NSF).

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COLL 136 Ultra-thin hafnium oxide atomic layer deposition on chemically prefunctionalized silicon

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The application of high-k dielectrics in microelectronics is stymied by the formation of interfacial SiO2. We have studied the role of surface chemical prefunctionalization in reducing silicon oxidation during HfO2 growth at moderate temperatures (~100oC), using tetrakis(ethylmethylamido) hafnium (TEMAH) and heavy water (D2O) as precursors. Using complementary surface/interface analytical techniques, such as infrared spectroscopy (IR), Rutherford back scattering spectroscopy (RBS), and medium energy ion scattering spectroscopy (MEIS), we show that no interfacial SiO2 is formed on hydrogen, chlorine, and silicon nitride passivated surfaces after HfO2 ALD. In situ IR studies reveal that interfacial SiO2 is formed only after post annealing above 500oC for HfO2–H/Si stacks, and 600oC for HfO2–SixNy stacks. Together with the appearance of interfacial SiO2, the initially amorphous HfO2 film begins to crystallize as evidenced by the appearance of a sharper HfO2 phonon mode at ~780 cm-1 and by the angular dependence in the MEIS.

COLL 137 The adsorption of biomolecules on alumina and silica substrates

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The use of solid oxides in drinking water purification is limited in some applications by the formation of biofilms. The biofilms can be initiated through the adsorption and lysis of cells on the oxide surface, coating the surface with biomolecules and passivating the surface for subsequent adsorption of intact cells. We are using vibrational spectroscopic techniques, FT-IR and FT-Raman, to examine the interaction of sucrose, as a model polysaccharide, with alumina and silica in aqueous solution. This study will provide important baseline information for the use of vibrational spectroscopy for the examination of the interactions of biomolecules with surfaces. The FT-IR and FT-Raman techniques provide complementary information for these studies. The initial results from this research effort will be presented.

COLL 138 The development of a colorimetric detector for the decomposition of dimethyl methylphosphonate on metal oxides

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The ambient temperature decomposition of dimethyl methylphosphonate (DMMP), an important chemical warfare agent simulant, on metal oxides typically generates methanol as the major product. The screening of a series of oxides for activity for the decomposition of this important chemical warfare agent simulant can be carried out in a combinatorial fashion if a means of assessing the effectiveness of an array of different solids for activity can be developed. The clearest assay for this type of application is one that involves a color change. We have developed an assay for the determination of the effectiveness of the metal oxide reactive adsorbents based on the enzymatic oxidation of methanol followed by the detection of formaldehyde using the reagent Purpald®, which changes color from colorless to purple when exposed to formaldehyde. Our results demonstrating the ability of this method to discriminate among reactive adsorbents will be presented.

COLL 139 Electrochemical modification of electrodes with in-situ generated diazonium cations

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The derivatization of a glassy carbon and gold electrode surface was achieved by electrochemical reduction of several in-situ generated diazonium cations. The diazonium cations were synthesized in the electrochemical cell by reaction of the corresponding amines with sodium nitrite in aqueous HCl. This deposition method, which involves simple reagents and does not require the isolation and purification of the diazonium salt, enabled the grafting of covalently bounded layers which exhibited properties very similar to those of layers obtained by the classical derivatization method involving isolated diazonium salt dissolved in acetonitrile or aqueous acid solution. Cyclic voltammetry and electrochemical impedance spectroscopy carried out in aqueous solutions containing electroactive redox probe molecules confirmed the barrier properties of the deposited layers. The chemical composition of the grafted layers was determined by X-Ray photoelectron and Infrared reflection-absorption (IRRAS) spectroscopies.

COLL 140 Resonance energy transfer in organic photovoltaic devices

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Resonance energy transfer (RET) has the potential to overcome a number of limitations associated with exciton transport in organic photovoltaic devices. Using dye-doped polystyrene blend films, we demonstrate that PCBM ([6,6]-phenyl C{sub 61}-butyric acid methyl ester) is an efficient resonance energy acceptor, despite the fact that its optical absorption is symmetry-forbidden. The implications of energy transfer in the performance of bulk heterojunction devices will be discussed in the context of photophysical results that show that RET leads to an increase in the apparent rate of exciton diffusion. We also report on the use of RET from P3HT (poly[3-hexylthiophene]) to a low bandgap polymer PTPTB (poly-N-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole), located near the electron-conducting electrode in a planar device. This directional resonance energy transfer efficiently places electrons at the exciton splitting interface, and yields a three-fold improvement in photocurrent. This work serves as a proof of concept for RET-based exciton harvesting, and introduces a new approach for photovoltaic cell design.

COLL 141 Separation of colloidal particles by electric field flow fractionation

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Microfluidics is rapidly becoming a very important area of research due to numerous potential applications in separations and analysis. The separation of charged particles in microchannels is frequently accomplished by applying electric fields either in the axial or in the lateral direction. In this poster we analyze the problem of separation of charged colloidal particles in DI water by lateral electric fields, i.e., Electric field flow fractionation. To model the separation in an EFFF device, one has to first predict the electric field in the microchannel. We solve the Poisson-Boltzmann equation along with the species conservation to predict the electric field and compare the results with experiments. Next, the calculated field is used to solve the convection diffusion equation for the colloidal particles. A multiple time scale analysis and regular expansions in the aspect ratio are used to determine the mean velocity and the dispersion coefficient of molecules in periodic EFFF. The averaged convection-dispersion equation is then used to predict the separation efficiency of EFFF devices. We investigate unidirectional and also periodic electric fields.

COLL 142 Structure and rheology of organoclay dispersions: Role of free surfactant

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We disperse organically modified montmorillonite clays [Cloisite® 15A (C15A) and Cloisite® 20A (C20A)] from Southern Clay Products in *p*-xylene. These clays differ from one another only in the fraction of surfactant added relative to the cation exchange capacity of the clay. Moreover, in order to study the effect of the free surfactant on the rheology and microstructure of the dispersions, we have removed free surfactant and created surfactant extracted analogues that we refer to as EC15A and EC20A. The quiescent character of the clay network has been characterized by XRD, TEM, and a novel wet-SEM technique. Mechanical rheological data are reported for dispersions with varying concentrations (1 to 4 wt%) of C15A, EC15A, C20A and EC20A. The samples were subjected to oscillatory and steady shear, and classic thixotropic behavior is observed in all cases, suggesting the existence of a three-dimensional gel-like, network structure.

COLL 143 rA mini Review on the progress of the synthesis and analysis of polymeric hydroxyl-aluminum in aquatic solution

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On the basis of reviewing the synthesis and identification of polymeric hydroxyl-aluminum, we summarize the progress on the synthesis and analysis of polymeric hydroxyl-aluminum in aquatic solution. The study of polymeric hydroxyl-aluminum in aquatic solution has a history as long as 100 years. Numerous investigations of the polymeric hydroxyl-aluminum in aquatic solution have led to the consensus that polymeric Al species, such as Al2, Al3, Al6, Al8, Al13, Al30 etc are present in the solution. In these species, Al2, Al13 and Al30 have been extensively studied [Namely, Al2(OH)2(H2O)8](SO4)2.2H2O, Al13O4(OH)24(H2O)127+ and (AlO4)Al28(OH)56(H2O)2618+]. The synthesize of polymeric Al and their analytical methods can be categorized as: (a) synthesis methods: base hydrolysis, acid dissolution, acid neutralization, thermal decomposition, electrolysis, and electrodialysis; (b) analytical methods: solid-state and solution 27Al NMR, conductometry, potentiometry, light-scattering, X-Ray diffraction, ultra-centrifugation, ion-exchange, dialysis technique, kinetic methods, theory model speculation and quanta chemical calculation.

COLL 144 Adsorption and photophysics of fullerene C60 on ultrastable zeolite Y

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This study reports unusually high affinity of fullerene C60 in toluene for ultrastable zeolite Y (USY). No comparable affinity for the zeolites NaX and NaY was found. The absorption spectrum of the ground and triplet states of C60 at the toluene-USY interface was similar to that in bulk toluene. Studies of singlet and triplet quenching show that C60 is located on the external particle surface of USY. While the driving force for C60 adsorption to USY is unclear, the effect is intriguing and provides a simple means by which to localize and organize C60 at the liquid-particle interface.

COLL 145 AFM measurements of adhesion between nanoparticles and substrate

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One of the key roles determining the final quality of a product involving nanoparticles is played by adhesion. Simple extrapolation of results obtained for model systems with particles size (even in micrometer range) is not always appropriate. Therefore, the best way is to determine the level of nanoparticle-surface or nanoparticle-nanoparticle interactions experimentally. To this end a method for measuring adhesion between nanoparticles and various substrates has been developed. Nanoparticles have been adsorbed and fixed on the surface using polymer anchoring layer. Atomic force microscope (AFM) operated in “force-volume” mode has been applied to measure the adhesion between silica nanoparticles and 30-40 µm hollow glass bead glued to the AFM cantilever. The influence of different factors (pH value, presence and concentration of surfactants) on the adhesion has been determined and compared with the literature data.

COLL 146 AFM measurements of adhesion between silica nanoparticles and poly(vinyl pyridine) layers

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In the present study adhesion between silica nanoparticles and ultra-thin poly(vinyl pyridine) (PVP) layers (thickness between 3 and 100 nm) was tested employing atomic force microscopy (AFM) in contact mode. PVP layers were deposited on silicon wafers by dip coating from solution. The nanoparticles were adsorbed (from water) on the substrate covered with the PVP film. The effect of polymer molecular weight and thickness of the layer on the adhesion was investigated. It was found that increase in the thickness had pronounced effect on the adhesion strength. Specifically, the

strength increased with the thickness dramatically. Increase of the adhesion strength with increase of molecular weight was also evident but less pronounced.

COLL 147 Alkyl phosphonate monolayers on hafnium-modified gold

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Control over the surface and interfacial properties of materials is essential to their integration into a number of applications, and a variety of surface functionalities are required to meet the needs of current and future materials modification. While thiol monolayers have been studied on gold surfaces, here we report the first modification of gold with an alkylphosphonate monolayer using a hafnium linker. Forming phosphonate monolayers on a conductive metal substrate offers a number of benefits. This chemistry makes possible the patterning of gold surfaces with rigid domains. This chemistry can also be used to modify metal and metal oxide surfaces concurrently, making it ideal for homogeneous functionalization of interdigitated arrays for numerous electronics applications. Here we report the initial discovery and characterization of alkylphosphonate monolayer assemblies on hafnium-modified gold. We demonstrate how hafnium patterned gold surfaces can be used in tandem with 2-mercaptoethylphosphonic acid to create a patterned surface.

COLL 148 Assembly of multilayers containing homopolynucleotides: A study of specific hydrogen bonding

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Assembly of homopolynucleotides, RNA's, into multilayers is performed via the layer-by-layer assembly protocol. Poly(adenylic acid), poly(A), and poly(uridylic acid), poly(U), were incorporated into a poly(ethyleimine), PEI, matrix following different polyelectrolyte deposition sequences. Build-up was investigated via ellipsometry, and atomic force microscopy. The latter revealed roughness variations depending on deposition order, 12 nm for $[\text{PEI/poly(A)/PEI/poly(U)}]_4$ and 30 nm for $[\text{PEI/poly(A)/poly(U)}]_7$. In addition, assembly was studied, in situ, by optical waveguide lightmode spectroscopy, OWLS, to elucidate the PEI/poly(A)/poly(U) interactions. Experiments show that the addition of poly(U) is a result of specific hydrogen-bonding between the nucleic bases of the latter and poly(A). Furthermore, the effect of ionic strength was analyzed by performing assembly from polyelectrolyte solutions of different salt concentration. Film thickness greatly depends on ionic strength, showing a decrease with increase in NaCl concentration, from 550 nm to 360 nm for build-ups performed, respectively, from 0 M and 0.8 M NaCl solutions.

COLL 149 Atomistic molecular dynamics simulation of the temperature and pressure dependence of local and terminal relaxation in amorphous polyethylene and cis-1,4-polybutadiene

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The dynamics of cis-1,4-polybutadiene (cis-1,4-PB) and polyethylene (PE) over a wide range of temperature and pressure conditions has been explored by conducting atomistic molecular dynamics (MD) simulations with a united atom model. Local dynamics in the two polymers has been analyzed in terms of torsion angle time autocorrelation functions (TACFs), and, in the case of cis-1,4-PB, also in terms of its dipole moment time autocorrelation function (DACF). By Fourier transforming the DACF for the simulated cis-1,4-PB system, the dielectric spectrum is computed and analyzed on the

basis of the time-temperature and the time-pressure superposition principles over the entire range of temperature (430 – 195 K) and pressure (1 atm – 3 kbar) conditions covered in the simulations. The relative contribution of thermal energy and volume to segmental and chain relaxation processes are also calculated and evaluated in terms of the ratio of the activation energy at constant volume to the activation energy at constant pressure, QV/QP. For cis-1,4-PB, computed QV/QP values lie between 0.74 and 0.97 (for the density range of 1.03-0.84 g/cm3 corresponding to the different temperature and pressure conditions studied here), in excellent agreement with recently reported experimental data based on time-resolved optical spectroscopy (Kirpatch and Adolf, Macromolecules 2004, 37, 1576-1582). Additional results for the temperature and pressure dependence of the Rouse times describing terminal relaxation in the two polymers show that, in the regime of temperature and pressure conditions covered here, segmental and chain relaxations are influenced similarly by pressure and temperature variations.

COLL 150 Biosensors using Maxi-K potassium channels in engineered tethered bilayer membrane arrays

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The demand for rapid in situ detection of chemical and biological analytes at high sensitivity has increased interest in the development of biosensors. Biosensors using ion channels have the potential to translate a molecular recognition event into a measurable current. In the case of stochastic sensing, the modulation of a single ion-channel's activity by an analyte is probed. Such sensing necessitates measuring single ion-channel events in the picoampere range. For stochastic sensing it is necessary to be able to measure the ion currents associated with single ion channel opening and closing events. By reconstituting the high conductance Maxi-K (*mSlo*) potassium channels into tethered bilayer lipid membranes on a microelectrode array device we were able to measure single channel activity. Additionally, the pharmacological response to known blockers for maxi-K, tetraethylammonium and charybdotoxin, were recorded using these biosensors.

COLL 151 C60/Gold nanoparticle hybrid films by layer-by-layer and in-situ cross-linking assembly

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Gold nanoparticles with a diameter of less than 10 nm have been synthesized and can be functionalized with various organic alkane- and arenethiolates. Aminothiophenol has been used as a protecting ligand in the formation of monolayer-protected nanoclusters. It is well established that C60 Fullerenes have strong affinity to amine moieties. Using this amination reaction, C60/Gold Nanoparticle Hybrid Films have been assembled via layer-by-layer and also by cross-linking assembly. These films have been characterized using Atomic Force Microscopy (AFM). The electrical and optical properties of this film such as the conductivity, resistivity, etc have been investigated. The thermal and ultrasonic stability of these films was also evaluated by monitoring the change in morphology during either heating treatments or ultrasonic irradiation treatments, respectively. A greater understanding of the properties of these hybrid films will ultimately lead to new device applications.

COLL 152 Calculating in-plane bending modulus of lipid bilayer edge

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We use coarse-grained molecular dynamics simulations combined with a Monte Carlo model to measure the energy due to the 1 dimensional in-plane curvatures existing in many systems such as lipid ribbons and bicelles. A mathematical model is used to interpret the curvature as a combination of independent modes each has equal energy of $k_BT/2$. From this study, the bending elasticity of 1 dimensional edge κ is 0.5~3e-28Jm for systems of various composition and edge length.

COLL 153 Characterization of some biopolymer-nanocomposite gels and solutions

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We are interested in developing and characterizing bio-nanocomposite soft materials containing guar gum type biopolymer (Carboxymethyl hydroxylpropyl guar) and the synthetic clay, Laponite (LRD). A feature which seems common in most successful preparations of clay based soft bio-nanocomposite materials is the presence of strong, specific interactions between the polymer and the clay for example via hydrogen bonding or ionic interactions. These interactions are responsible for large scale structures that in return are capable of forming viscoelastic soft materials at very low concentrations. The viscoelastic behavior of such a biopolymer clay hydrogel depends on parameters such as the type of biopolymer, the concentration, polymer molecular weight, pH, and salt concentration. The strength of the hydrogel is strongly related to the polymer-clay interactions. Here we are presenting the viscoelastic behavior of a series of bio-nanocomposite gels and solutions made from biopolymer and clay in order to understand the shear alignment of the large scale structures that build up and break during flow.

COLL 154 Characterization of the M2δ oligopeptide ion channel mutant in an artificial lipid membrane

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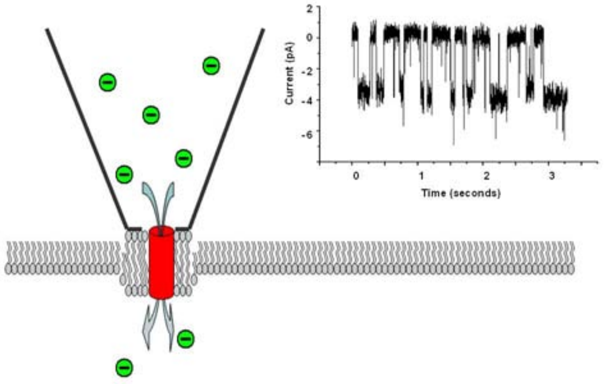
Ion channels are proteins that regulate the extra and intracellular ion concentration by mediating the passage of ions. The M2δ ion channel is a bundle of self-assembling transmembrane α-helices based on the pore lining region of the nicotinic acetylcholine receptor (nAChR). Recent techniques have been developed to allow the formation and measurement of single ion channels embedded in synthetic lipid bilayers. Oligomeric assembly of the M2δ ion channel produces stochastic behavior suitable for characterization. Utilizing tip-dip patch clamp technique, we were able to analyze this activity when known potentials were applied across the bilayer. Preliminary pharmacological studies have indicated that Triethyl Phosphate (TEP) affected ion channel activity, including the open-close probability and current amplitude. This proves to be a promising step towards the manipulation of M2δ ion channel activity and may be applied to other pharmacological agents.



COLL 155 Chemical modifications of multi-walled carbon nanotubes

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Carbon nanotubes are of considerable interest because of their unique physical and electrical properties. We report our results on the chemical modification of multi-walled carbon nanotubes. Following the introduction of carboxyl groups, we have carried out acylation and amidation reactions, and upon reduction, Grignard reactions.

COLL 156 Chemo-/bio-orthogonal immobilization of biomolecules onto solid surface

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In this presentation, we demonstrate that sequential aqueous Diels-Alder and click chemistry provide a facile route for the immobilization of biomolecules such as protein and carbohydrate onto a solid surface in a chemically and biologically orthogonal manner. In detail, a versatile heterofunctionalized poly(ethylene glycol) (PEG) crosslinker carrying an alkyne group at one end and cyclodiene at the other chain terminus was synthesized and immobilized onto an N-(e-maleimidocaproyl) (EMC)-functionalized glass slide substrate via an aqueous Diels-Alder reaction first. In the process, an alkyne-terminated PEGylated surface was provided for the conjugation of azide-containing biomolecules via click chemistry that proceeded to completion at low temperature and in aqueous solvents. Successful immobilization of an azide containing sugar and recombinant protein was confirmed by confocal microscopy after FITC-labeled specific sugar/protein-recognizing protein binding. Significantly, the click reaction proceeds to completion at low temperature and in aqueous solvents. In particular, azide, alkyne, cyclodiene and EMC are stable under bioconjugation conditions and are not predisposed to unintended side reactions. Therefore, the potential to immobilize a wide range of functionally complex substances onto a solid surface can be achieved, which will likely extend the applications of microarrays and medical devices whose performance is dictated by the molecular engineering of precisely defined interfaces.

COLL 157 Coalescence of heterogeneously nucleated charged droplets

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Heterogeneous nucleation of a liquid results in a collection of growing droplets. As nucleated droplets grow on a surface, they come closer together and interact, leading to either coalescence or in-plane rearranging motion maintaining an interface separation. In the latter case, continued growth of multiple droplets on a substrate of finite size should eventually yield a packed configuration which prohibits subsequent droplet rearrangement. In this confined state, droplet behavior could proceed via continued deformed or undeformed growth, and possible coalescence. We develop a thermodynamic theory that uses interaction energies between two identical droplets to predict the fate of heterogeneously nucleated, growing droplets., The theory is used for an example system to develop criteria that determine whether the initial droplet configuration results in coalescence or transition to a packed configuration, and, in this latter configuration, whether the droplets will deform, and if they will coalesce.

COLL 158 Concentration and ionic strength effects on peptide adsorption at the solid/liquid interface investigated by sum frequency generation vibrational spectroscopy

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The effect of parameters such has the ionic strength of the solution and the concentration of an amphiphilic peptide in solution on its adsorption behavior is poorly understood. In this study, Sum Frequency Generation Vibrational Spectroscopy (SFG-VS) has been used to examine the adsorption of the peptide Ac-LKKLLKLLKKLLKL-NH2 (L=Leucine; K=Lysine) on hydrophobic polystyrene and hydrophilic silica as a function of the ionic strength of pH 7.4 phosphate buffer saline (PBS). On hydrophilic silica, an N-H mode was observed upon adsorption from a 0.01 M PBS solution, whereas no such mode is present at 0.0001 M. Instead, strong signal from interfacial water molecules is observed. The effect of peptide concentration on the interfacial adsorption behavior was also investigated and compared for similar isosequential peptides, Ac-ARRAARAARRAARA-NH2 (A=Alanine; R=Arginine) and Ac-FRRFFRFFRRFFRF-NH2 (F=phenylalanine). From SFG, we observed that adsorption shows a strong dependency on both the peptide concentration and the buffer concentration.

COLL 159 Coning effect in dynamic light scattering of light absorbing colloids

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Heating is a basic phenomenon that occurs when light absorbing colloidal solutions are illuminated with a laser beam. Local heating changes the refractive index along the beam path creating a thermal lens. Consequently, the geometry of the laser beam changes from cylindrical to conical. In dynamic light scattering experiments, the divergence in the laser beam results in a coning angle, which should be considered in calculating the scattering vector. To explore the coning effect, a colloidal mixture of polystyrene and coated silica particles dissolved in a medium that absorbs the incident light was prepared and studied. The coning angle was calculated from the digital image of the laser beam and was compared with the values of the coning angle that were extracted from the q dependence of intensity-intensity autocorrelation functions. Laser power and dye concentration were varied so as to control the coning angle. The effect of coning on the determination of diffusion coefficients using dynamic light scattering was considered.

COLL 160 Convergent synthesis of poly(methyl methacrylate) (PMMA) based electroluminescent colloids

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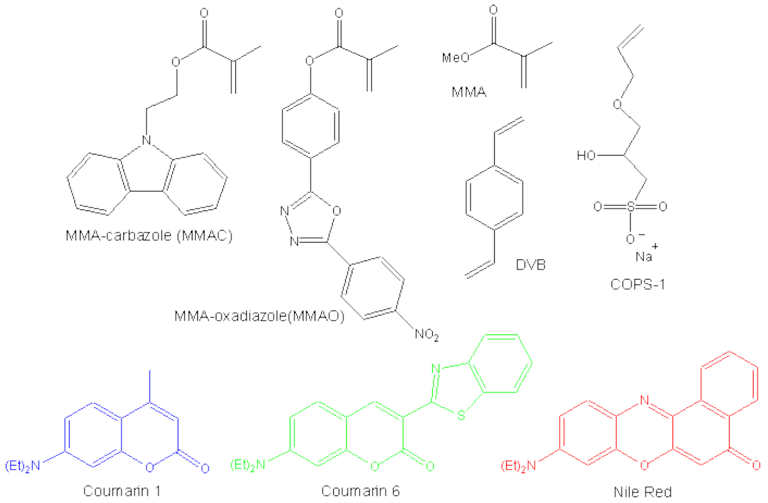
The development of small-molecule based, organic light emitting diodes (OLEDs) has received a great deal of attention in recent years as versatile alternatives to inorganic based LED systems. Here we report the convergent synthesis of all-inclusive PMMA based electroluminescent colloids using an emulsion polymerization technique. This multi-component colloid was synthesized from methyl methacrylate (base polymer), methacrylate functionalized carbazole (2-(9H-Carbazol-9-yl)ethyl methacrylate (MMAC), hole-transport molecule), methacrylate functionalized oxadiazole (2-(3'-Nitrophenyl)-5-(4'-methacryloylphenyl)-1,3,4-oxadiazole (MMAO), electron-transport molecule), and Coumarin 6 (electroluminescent dye). Emulsion polymerization of these multi-component LED colloids results in the formation of monodisperse particles (~ 100 nm) containing an interchangeable electroluminescent dye en route to the design of all polymer colloid based PLED devices.



COLL 161 Deposited polydiacetylene colloids for fluorescence based detection of microorganisms

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We have produced fluorescent polydiacetylene (PDA) coatings by depositing various aqueous colloidal diacetylene solutions onto nanoporous filter membranes followed by photopolymerization. PDA is a conjugated polymer that changes its fluorescence state in response to environmental perturbations such as pH, temperature, etc. The polymer coating, when conjugated to a biological recognition element, creates a surface that can respond to the presence of selected microbes. Integration of fluorophores into the coatings has been demonstrated to increase the emission signal via energy transfer. We have tested different types of membrane surfaces and the effects of different pretreatments on the integrity of the coatings. The coated filters can both concentrate and detect microorganisms at the surface. Incorporated antibodies and other ligands serve as biological recognition elements, which in turn transduce binding events into measurable alterations in the fluorescence of the PDA. The response of various coating formulations to selected model organisms is demonstrated.

COLL 162 Design of chemical structure of surfactant for aqueous dispersion of single-walled carbon nanotubes

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The effect of chemical structure on the aqueous dispersion properties and solubility of single-walled carbon nanotubes (SWCNTs) was investigated with an emphasis on the chemical control of the head and tail group in the surfactant. The dispersibility properties of SWCNTs were characterized using optical spectroscopy (UV-Visible spectroscopy) and electrokinetic dynamic mobility as a function of chemical structure of surfactants. Correlation was made between dispersion of SWCNTs and chemical structure of surfactant. It was found that ionic-fluorinated surfactant is much more effective than other surfactants to disperse SWCNTs in an aqueous medium through a combination of steric and electrostatic interparticle repulsive forces. The optimal chemical structure of surfactant for effective dispersion of aqueous SWCNTs will be proposed.

COLL 163 Dynamic interfacial tension in oil-water systems

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Interfacial tension is an important property of immiscible systems consisting of two liquid phases. In systems composed of pure oil, such as octane, and pure water, the interfacial tension is essentially constant. Most real-life oil-water systems found in both nature and industry do not fall into that simple category. Often, surface-active substances are present. Of particular interest is the case in which a surfactant is produced in-situ through a chemical reaction, taking place at the interface. This is the case, for example, in alkaline oil recovery where a solution of alkali interacts with oil-borne acids. The oil-water tension at the interface is then dependent on time. When the reacting interfaces are continuously moving and changing, the interfacial tension becomes dynamic. The behavior of such a flowing two-phase system is hard to predict and simulate. In this presentation, dynamic interfacial tension phenomena will be illustrated using examples of oil displacement work conducted in the author's laboratory.

COLL 164 Effect of composition on formation and growth mechanism of CdS nanoparticles in microemulsion

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Nanoparticles of CdS are synthesized by mixing two AOT microemulsions containing cationic and anionic precursors at room temperature. The particle sizes and distributions of microemulsions of different water to surfactant molar ratio (W) and oil phase are measured by analyzing UV-vis absorption spectra. The formation and growth mechanisms of CdS nanoparticles are investigated by comparison of the spectra at various times. The mechanism is varied with the W values and the type of oil phase. The mechanism variation is discussed in terms of kinetic behavior of microemulsion droplets.

COLL 165 Effect of introduced molecules on characteristics of capsule's membrane composed of polyelectrolytes

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Capsules are used in controllable release of drugs and immobilization of cells and enzymes. It is an important method of capsule formation by the reaction between polyelctrolytes. Sometimes it is necessary to improve the membrane characteristics of capusles due to the application requirement. In our work, the membrane characteristics of capsules composed of sodium cellulose sulfate (NaCS) and poly[dimethyl(diallyl)ammonium chloride] (PDMDAAC) was investigated under the condition of introduction other molecular. The small molecule, soluble polymers, soluble polyion and salt of small molecule were individually added into polyanion (NaCS) solution to check their effects on capsule formation. The membrane thickness and mechanical intensity of capsules were studied under the condition of different concentration of molecular added. Simultaneously the effects of molecular added on viscosity and Zeta potential of dilute NaCS solution were investigated. The study indicated that effects of additional molecular on the membrane characteristics could be judged by viscosity and Zeta potential variation of dilute polyectrolys.

COLL 166 Effects of Na+ Cloisite clay on polyurethane dispersions

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There has been much interest in enhancing the properties of polymer materials in academia as well as in industry. One such method is to add inorganic clays, especially in such a way as to result in their being fully exfoliated. Incorporation of inorganic material can improve mechanical properties, thermal resistance, barrier properties and chemical reagent resistance. These improvements yield low cost high performance materials. In this work, the gelation of aqueous polyurethane dispersions will be studied. The gelation is most likely caused by ion exchange between the surface of the clay and the ionic groups of the polyurethane dispersions. A series of formulations which addressed a range of clay concentrations vs. dispersion were prepared and studied as a function of time after preparation. These materials were characterized by X-ray diffraction, thermogravometric analysis, and rotational viscometry to determine the overall placement of the clay structures within the PU solutions and films made there from.

COLL 167 Effects of the fluid density and water-to-surfactant ratio on reversed micelle formation in supercritical carbon dioxide

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We examined the effects of temperature, pressure, and molar water-to-surfactant ratio on the fluorinated surfactant reversed micelles in supercritical CO_2. Through the measurements of FT-IR spectrum and dynamic light scattering, the reversed micelles were found to shrink with increasing the pressure and to swell with increasing the ratio. The area occupied by one surfactant molecule, which was given by the water/CO_2 interfacial tension measurement, suggested to the fluorocarbon tails be well expanded with an increased CO_2 density.

COLL 168 Electrokinetic-hydrodynamics: A useful framework to conduct research and trainning

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Electrokinetics (EK) has been around from the time of the electrical phenomena discovered by Volta, Galvani, Arrhenius, Ostwald, Nerst and others. In today technology, EK has gained a forceful presence since applications on genomics, proteomics, micro-separations, electrophoresis, fuel cells just to name a few are at the heart of many new technologies. Therefore, there is a need for

students to be trained in areas where EK plays an important role. A need for systematization has been recognized recently (see Saville, 2004).

Based on the framework of the successful transport theory introduced by Bird, Stewart and Lightfoot (1960) and a definition of electrokinetics based more on electrical engineering rather than on colloidal chemistry, the authors will present a framework for the understanding of the subject including identifying the word “Electrokinetic-Hydrodynamics” to highlight a family of applications where both EK and hydrodynamics play a substantial role. Furthermore, the authors will identify a number of analogies with non-electrical applications that helps students/new researchers to quickly grasp concepts and put them to work in their research or profession. The experience gained at the FAMU-FSU College of Engineering, Tennessee Tech College of Engineering and the College of Engineering at the Universidad Catolica del Norte in Antofagasta, Chile and workshops delivered at international meetings for practitioners by one of the authors (PA) will be used as feedback.

COLL 169 Electrospinning frozen in time

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Electrospinning is known to produce microfibers with small diameter and/or high surface area. Often times, the high surface area of these fibers is associated with their surface structures, consisting of nanometer-sized holes, droplets, or microcups, whose formation depends on the spinning condition and the type of the solutions used.

A mixture of isotactic and syndiotactic PMMA in dimethyl formamide was used in our study to produce helical microfibers by electrospinning at elevated temperatures. Rapid cooling during electrospinning allows for fast physical gelation to take place and trap helical microstructures arising from instabilities due to electrostatic, capillary and viscous forces.

The formation of these helices was considered in terms of stability theory for electrically forced jets.

COLL 170 Electrostatically driven critical aggregation behavior in layer-by-layer complexes of an anionic surfactant and an oppositely charged polyelectrolyte

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Complexation between sodium dodecyl sulfate (SDS) and poly(ethyleneamine) (PEI) in electrostatically bound multilayers was studied as a function of surfactant concentration. Multilayer films were fabricated using the conventional layer-by-layer (LbL) approach in which a repeat trilayer scheme of [PEI/SDS/PAZO]n (n = 1 to 10; PAZO: (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]) was constructed. In the LbL assemblies, SDS was adsorbed from concentrations ranging from 10-6 mM to 0.1 mM to investigate complexation in the composite multilayers. A reduction in overall film thickness and PAZO packing density was observed in the films as the concentration of SDS increased. The critical aggregation concentration (cac) of the PEI-SDS system was determined using surface tensiometry. We describe an electrostatically driven PEI-SDS complexation process in LbL films similar to the polymer-assisted micellization observed in the bulk aqueous phase.

COLL 171 Exploration of peptide-gold interfaces using surface enhance Raman scattering (SERS)

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Many groups have hypothesized that short (<20aa) peptides can be used for the delivery of metal nanoparticles to specific targets for either biomedical or nanofabrication applications. Though, several groups have been successful in the selection of peptides that will specifically bind to metal and semiconductor surfaces from biological / combinatorial libraries (phage, bacterial, and yeast displays), there has been limited discussion of the mechanism of binding between peptides and such surfaces. Our group has recently focused on the use of molecular spectroscopy (namely, surface-enhanced Raman scattering) to study peptide-metal interfaces to help elucidate the binding mechanism of “gold-specific” peptides isolated by other groups from biological, phage or yeast display systems. The goal of this project is to understand the molecular basis of this binding in order to improve upon the evolutionary technique used by others and design peptides for directed delivery of nanoparticles to specific biological targets.

COLL 172 Fabrication of mixed monolayers and their built-up films containing comb polymers with hydrocarbon or fluorocarbon side-chains

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Mixed monolayers of comb polymers having hydrocarbon or fluorocarbon side-chains with fluorinated or hydrogeneted amphiphiles, respectively, on the water surface were examined with view points of their miscibility and/or the phase separation from the surface pressure - molecular area isotherm measurements and also those lateral packing structures of the mixed monolayers transferred on solid substrates were studied by an in-plane X-ray diffraction and an atomic force microscopy. The extremely fundamental results of the mixed films of comb polymers are available for the controlled topography of molecular substrates with various nanostructures. Those mixed films are expected to give well-defined chemical templates in order to organize some complex dyes, functional polymers and biomolecules in the following potential application.

COLL 173 Friction force measurements of polystyrene brushes in various solvent environments

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Polystyrene brushes were prepared on oxide passivated silicon by the surface initiated polymerization technique. The 4,4'-azobis(4-cynanovaleric acid) free radical initiator was silanized and immobilized on silicon wafers from which polystyrene was directly grown. The formation of the initiator film, and, subsequently, the polymer brush on the surface were tracked by X-ray photoelectron spectroscopy (XPS) and by ellipsometry. Friction force measurements were performed by atomic force microscopy (AFM), using a 0.5 micron SiO_2 colloidal sphere tip, and continuously under various solvent environments (polar to non-polar, and vice versa), to demonstrate the dependence of brush lubricity on solvation.

COLL 174 Functionalization of citrate-stabilized gold nanoparticles with ligands featuring charged organic groups

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Gold nanoparticles can serve as components of new nanoscale devices due to their size dependent optical and electronic properties. Particles formed via the reduction of Au(III) salts by trisodium citrate are of particular interest, for their simple preparation method offers access to a wide range of particle sizes. Modification of the particles surface functionality by the addition of a thiol based ligand shell further increases their utility in nanoscale devices, facilitating self assembly processes by imparting stability in various aqueous and organic solvent environments.

COLL 175 Genetic manipulation of an icosahedral plant virus for the fabrication of functional nanoparticles

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Due to their fascinating structural features, viruses have recently been explored as components of hybrid inorganic materials, as molecular entities for chemical reactions, and as templates to construct ordered nano-composites. In the present study, turnip yellow mosaic virus (TYMV) has been employed as a nanoscale scaffold for genetic and chemical modification. The TYMV coat protein was modified genetically by cloning methods in order to insert functional groups such as thiols, carboxylic acids, and phenols on the exposed loops of the capsid protein. In addition, foreign peptides have also been inserted on the exterior surface of TYMV for cell binding studies. The modified TYMV was propagated in turnips by making the infectious RNA by reverse transcription, and the results were confirmed by RT-PCR analysis of the mutants of TYMV. Our study has shown that functional motifs can be programmed into TYMV genetically which leads to its further application in materials development.

COLL 176 Glutathione-mediated drug release using monolayer protected nanoparticle carriers

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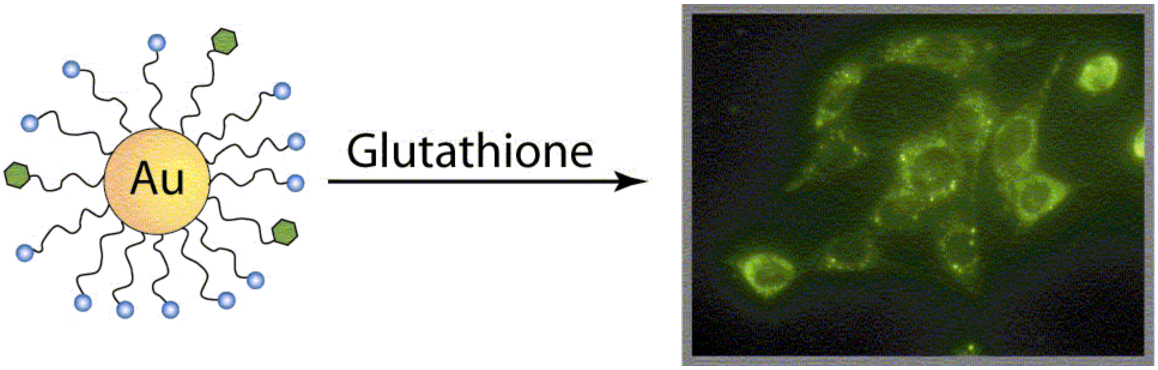
Mixed monolayer protected gold clusters (MMPCs) were developed as excellent drug delivery systems, using a unique glutathione-mediated release mechanism. Both in vitro and in vivo releases of dye (drug) payload from nanoparticle surface were established. Furthermore, glutathione-monoester served as an external stimulus to successfully trigger drug release, enhancing the applicability of controlled drug delivery and release using nanoparticle carriers. The GSH-mediated release, combining with the controlled interactions of biomolecules with surface functionalized nanoparticle scaffolds, can be further utilized to realize delivery of proteins and enhance transfection of genetic materials.



COLL 177 Group transfer polymerization synthesis of amphiphilic model conetworks based on methacrylic acid

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Model amphiphilic conetworks containing tetrahydropyranyl methacrylate (THPMA) (later modified to methacrylic acid) were synthesized using group transfer polymerization (GTP). In particular, two groups of amphiphilic co-networks were prepared, the first one using methyl methacrylate (MMA) and THPMA and the second one using 2-butyl-5-octyl methacrylate (BOMA) and THPMA. 1,4-bis(methoxytrimethylsiloxymethylene)cyclohexane (MTSMC) and ethylene glycol dimethacrylate (EGDMA) were used as the initiator and the cross-linker, respectively. Network synthesis was performed by sequential monomer / cross-linker additions to the reaction flask which was pre-loaded with catalyst, solvent and initiator. All network precursors and the extractables were characterized in organic solvents by gel permeation chromatography and nuclear magnetic resonance spectroscopy to determine the molecular weights and compositions, respectively. Subsequently, the THPMA units were hydrolyzed to MAA units and the polymer conetworks were characterized in terms of their degree of swelling in aqueous media as a function of solution pH and in organic solutions.

COLL 178 High performance OLEDs fabricated by layer-by-layer deposition of terthiophene and CdS nanoclusters

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Oligothiophenes have remained one of the most interesting materials because of their potential applications in organic electronic devices such as organic light emitting diodes (OLEDs). Moreover, the optical and electronic properties of oligothiophenes can be easily tuned by changing either substituents or microstructures. Semiconductor nanocrystals or quantum dots such as CdS and CdSe and their composites with organic molecules have been extensively investigated recently in nanoscience and nanotechnology. Different shapes and sizes of CdSe nanocrystals have been used as active components of light-emitting diodes and photovoltaic cells. Because of the properties of semiconducting conjugated polymers and inorganic semiconductor nanocrystals are similar for used as electronic devices, therefore the new semiconductor materials should be created from these composites. In this work, high performance OLEDs were fabricated by alternate deposition of CdCl2 and dithiol functionalized terthiophene with subsequent reduction by Na2S. This layer-by-layer technique is especially promising because it overcome the problem of trapping ion pairs salts in thin films.

COLL 179 Horse spleen ferritin as building block for chemoselective modification and self-assembly

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Ferritin and apoferritin have been employed as nanoscale building blocks for new materials development. In this work, we investigate the chemo- and regio-selective modification of ferritin and apoferritin. In particular, succinimide derivatives are used to modify the lysine groups; and amine derivatives are used to conjugate on carboxylic acid residues on the surface of ferritin and apoferritin. MALDI-TOF analysis and proteomics methods are used to identify the reactivity and selectivity of the reactions. Furthermore, alkyne and azide groups have been attached on the surface of ferritin, which can be further derivatized by copper (I) mediated 1, 3-dipolar cycloaddition

reactions. Therefore, ferritin and apoferritin can be considered as robust building blocks for chemical modifications. The functionalized ferritins have been further used in self-assembly studies. For example, polyethylene oxide (PEO) tailored ferritin has been applied in the co-assembly study with diblocks copolymers.

COLL 180 In situ scanning tunneling microscopy studies of bimetallic cluster growth: Pt-Rh on TiO2(110)

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The growth of Pt-Rh bimetallic nanoclusters, formed by depositing Pt on 0.3ML of Rh predeposited on a TiO2(110) surface, has been investigated using scanning tunneling microscopy (STM) and low energy ion scattering (LEIS). In situ STM studies during Pt deposition show that bimetallic nanoclusters are produced by direct incorporation of Pt atoms into existing Rh clusters or coalescence of nucleated Pt clusters with predeposited Rh clusters. Cluster densities for Pt-Rh growth are lower than those for pure Pt growth, suggesting that the Rh clusters act as nuclei (seed clusters) for the formation of Pt-Rh bimetallic clusters. In situ STM studies at 100K and 450K clarify the Pt-Rh growth kinetics based on the different adatom diffusion rates. LEIS experiments show that Pt does not completely cover the surfaces of the Rh clusters even at the highest Pt coverage, suggesting that Rh atoms can diffuse within the Pt-Rh bimetallic nanoclusters.

COLL 181 In situ vibrational spectroscopy of thin organic films confined at the solid-solid interface

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Thin organic films confined between an optical prism and an optical lens have been studied with Raman scattering and sum-frequency spectroscopy. Sum-frequency spectra of a single monolayer of zinc arachidate deposited on a prism have been recorded during and after contact with a lens. The lens was used to apply pressures of 30 MPa to 200 MPa and spectra were also obtained under sliding contact with the lens. The conformationally ordered Langmuir-Blodgett (LB) monolayers of zinc arachidate retained their high degree of order under conditions of pressure and shear, but changes in peak frequency and peak intensity were observed. Conventional modeling can currently explain some of these observations. Raman scattering has also been used to study thin liquid films at the solid-solid interface.

COLL 182 In-situ adsorption studies of a 14 amino-acid leucine-lysine peptide onto hydrophobic polystyrene and hydrophilic silica surfaces using sum frequency generation vibrational spectroscopy, atomic force microscopy, and a quartz crystal microbalance

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The adsorption of a 14-amino acid amphiphilic peptide, composed of leucine (L, apolar) and lysine (K, charged), on hydrophobic polystyrene (PS) and hydrophilic silica (SiO2) was investigated by Quartz Crystal Microbalance (QCM), Atomic Force Microscopy (AFM), and Sum Frequency Generation (SFG) Vibrational Spectroscopy. QCM adsorption data revealed that the peptide adsorbed onto hydrophobic PS through a fast (<2 min) process, while a much slower (~30 min) multi-step adsorption and rearrangement occurred on the hydrophilic SiO2. AFM measurements showed different surface morphologies and friction coefficients for LK14 adsorbed on the two surfaces. SFG spectra indicate significantly different ordering of the adsorbed peptide on the two surfaces: at the PS/peptide solution interface, C-H stretches corresponding to the hydrophobic leucine side chains are evident; while N-H stretches are observed at the SiO2/peptide solution interface. The molecular data provided by SFG-VS is compared to the macroscopic data observed with QCM and AFM.

COLL 183 Incorporating calcogenide (CdS, ZnS, PbS and Ag2S) nanocrystals into silica nanospheres for photonic applications

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Methods for synthesizing monodisperse calcogenide@silica core-shell composite nanoparticles were developed. CdS, ZnS, PbS and Ag_2S were incorporated into silica spheres by one-step reaction in the microemulsion medium. Silica nanospheres were formed by hydrolysis of tetraethoxysilicate using NH_3 as a catalyst, while calcogenide nanocrystals were produced in situ by chemical precipitation of metal ions (Cd^{2+}, Zn^{2+}, Pb^{2+} or Ag^{+}) with S^{2-} in the microemulsion. These calcogenide nanocrystals could be embedded inside SiO_2 spheres either as homogeneously dispersed quantum dots or centered single cores. The calcogenide@silica nanospheres were found to have a narrow size distribution, and their sizes could be tailored for various applications such as the optical properties of the dispersions may be controlled by varying silica shell thicknesses. By further enhancing the surface charge density on silica, these monodispersed shell-core particles could self-assemble into colloidal photonic crystals in pure water. The colloidal phoronic crystals efficiently Bragg-diffracts light in visible and near-IR regions, depending on the size and number concentrations of nanospheres in suspension. These new photonic crystal materials have potential applications in nonlinear optical limiters and nonlinear optical switches.

COLL 184 Influence of alginate on the eletrokinetic properties and aggregation kinetics of hematite nanoparticles

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Alginates are polysaccharides that are ubiquitous in natural and engineered aquatic systems. It is likely that alginates adsorb to metal oxide nanoparticles in these systems significantly affecting the surface characteristics of these nanoparticles. We examined the affects that alginate has on the electrokinetic properties of hematite nanoparticles, and observed important differences in the zeta potentials of these particles with time of alginate absorption. Zeta potentials become increasingly negative with increasing pH until pH > 11.5 were this trend shifts to less negative zeta potentials. In parallel studies, the aggregation kinetics of the alginate-coated hematite colloids is measured in monovalent and divalent electrolytes by dynamic light scattering. The growth rate of the aggregates in the presence of some divalent cations is much faster than in either magnesium or sodium chloride, and can be faster than diffusion controlled kinetics predict. The mechanism for this enhanced aggregation will be discussed.

COLL 185 Interaction between modified polyethersulfone surfaces functionalized with blood composition

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It is important to research interaction between material surfaces with blood for improving the hemocompatibility of biomaterials.Medical grade PES was selected for original material, 1,12-Hexanediamine was served as space arm to covalently link heparin to form a novel biomaterial. The interaction between modified polyethersulfone surfaces functionalized with blood composition was investigated by means of testing surface properties incuding albumin adsorption,plasma total protein and globulin count,platelet adhesion ,platelet count,red cell dissolving, coagulant factors and calculation of surface free energy. The adsorption of plasma proteins and the adhesion of platelet were compared on the surfaces, H-PES was in favor of increasing the quantity of albumin comparing to original PES. Lower platelet adhesion was observed on the H-PES surface. The amount of platelet adhered on H-PES surface reduced by 55% compared with PES. The results indicated that on heparinized PES surface with algoid structure indeed appear possessing good antithrombogenic proterties.

COLL 186 Interaction of hydrolyzed collagen with amphoteric nanoparticles

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It is well known that substantial improvements in mechanical properties can be realized by incorporation of nanoparticles into polymer matrices. This study was directed to the enhancement of collagen films and fibers by smectite clays. The amount of collagen incorporation into montmorillonite clays was determined by construction of adsorption isotherms; the extent of adsorption by hydrogen bonding was probed by measuring absorbance wavelength shifts by FTIR; the adsorbed collagen conformation was estimated by proton NMR peak broadening and the extent of intercalation and exfoliation was measured by small angle X-Ray diffraction. Exfoliation was achieved in most instances within tight boundary conditions of pH and ionic strength. The mechanism of adsorption and intercalation was explained in terms of enthalpies of adsorption and the relative conformations of the collagen in solution state and adsorbed state.

COLL 187 Investigation of electrochemical copper patination on noble metal surfaces

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Patination can be defined as the process of forming a film or incrustation by the chemical alteration of the surface resulting in color change. In less acidic environment (ca. pH 5-6) of copper sulfate plating solution, it has been found that a thin coating of crystalline precipitate is formed on noble metal electrodes at potentials ca. + 0.21 V vs. Ag/AgCl reference electrode. Analyses of this electrochemical deposit by (i) XRD, (ii) XPS (iii) cyclic voltammogram and (iv) mass changes by EQCM (Electrochemical Quartz Crystal Microbalance) have confirmed that the thin crystalline coating is a type of basic copper sulfates, which is chemically identical to “posnjakite”, a type of Cu patina deposits. Based on the new findings, the detail reaction mechanism of electrochemical Cu patination process will be present.

COLL 188 Investigation of the effects of electrolyte concentration and electrolyte addition order on complex coacervate formation

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Complex coacervates are useful in a variety of applications, including controlled release drug delivery and conditioning agents in personal care products. Complex coacervate formation is a result of the interactions of two macromolecules, or a macromolecule and an association colloid, each carrying an opposite charge. The current investigations involve a rigid cationic cellulosic polymer with anionic surfactant and a monovalent salt. The effect of electrolyte concentration on complex coacervate formation was investigated using high-throughput screening methods that were developed to explore these interactions with varying electrolyte concentrations. In addition to salt concentration studies, a salt concentration gradient was employed to examine the effect of electrolyte addition order on complex coacervation. The effects of salt concentration and addition order on coacervate formation are complex. Likely mechanisms will be advanced to explain the complexities.

COLL 189 Investigation of the effects of hydrophobic substitution on complex coacervate formation

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Complex coacervates are useful in a variety of applications, including controlled release drug delivery and conditioning agents in personal care products. Complex coacervate formation is a result of electrostatic interactions between two macromolecules, or a macromolecule and an association colloid, each carrying an opposite charge. Subsequent to the electrostatic interactions, hydrophobic associations can occur between tail groups of bound surfactant molecules. Therefore, the introduction of a hydrophobic moiety to a polymer backbone could influence the amount of coacervate formed. In this research, high-throughput screening formulation methods were used to explore the changes in coacervate with the addition of hydrophobic moieties. Cationic cellulosic polymers were used, with variations in hydrophobic substitution. Compared to the unmodified polymer, only a small change in coacervation was seen with the addition of a low amount of hydrophobe. Increasing the degree of hydrophobic substitution caused an increase in coacervation over a wide range of concentrations.

COLL 190 Investigation of the phase behavior for microemulsion systems by renormalization-group theory

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The repulsive interaction between microemulsion droplets is expressed by an improved Carnahan-Starling equation where the deformation of microemulsion droplets is taken into account. The attractive interaction is expressed by three kinds of potentials: square-well, Yukawa and Lennard-Jones potentials. The energy parameter is expressed as the function of temperature. By using the established equation of state (EOS) and the renormalization-group (RG) theory, the liquid-liquid phase equilibria for microemulsion systems are studied. The phase splitting point is determined. The obtained results agree well with the experimental data of Sodium bis(2-ethyl-hexyl)sulfosuccinate (AOT) microemulsion systems.

COLL 191 Investigation of the polyelectrolyte-association colloid interactions in the semi-dilute and concentrated regime using high-throughput screening

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Complex coacervates are useful in a variety of applications, including controlled release drug delivery and conditioning agents in personal care products. Complex coacervate formation has been studied extensively in the dilute surfactant regime, and is known to be a result of the interactions of two macromolecules, or a macromolecule and an association colloid, each carrying an opposite charge. A commercially available cationic poly(acrylamide) was complexed with an anionic surfactant and the interactions were investigated using high-throughput screening formulation methods. These methods were used to investigate coacervate formation by rapidly constructing multi-component phase diagrams covering a wide range of polymer and surfactant concentrations. The multi-component phase diagrams served as a guide to compositions of particular interest, which were studied in more detail to determine coacervate structure, size and charge.

COLL 192 Kinetics and viscoelastic behavior of layer-by-layer alternately deposited polyelectrolyte multilayers: Quartz crystal microbalance and surface plasmon resonance studies

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Self-assembled multilayers composed of alternating layers of poly(diallyldimethylammonium chloride) (PDADMAC) and poly[1-[4-(3-carboxy-4-hydroxy-phenylazo)benzenesulfonamido]-1,2-ethanediyl, Sodium salt] (PAZO) were studied by quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) spectroscopy. QCM provided the in situ change in frequency and resistance simultaneously. The kinetic properties of adsorption for different concentrations of PDADMAC and PAZO have been examined up to 3 bilayers. Both QCM and SPR results showed comparable sequential growth of the LBL films. The mass of polymer in each adsorption step was determined by QCM after the films were exposed to corresponding polymer solutions. Furthermore, the relationship between the frequency change and the resistance change during adsorption was investigated in order to study the fundamental properties of adsorption. The viscoelastic behavior or energy dissipation properties of surface bound LBL films of PDADMAC and PAZO will be assessed using QCM-dissipation experiments.

COLL 193 Lipid bilayer membranes supported by hydrogel

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We have encapsulated lipid bilayer membranes within a PEG-DMA (polyethylene glycol dimethacrylate) hydrogel. The lifetime and mechanical stability of these hydrogel encapsulated membranes (HEMs) are far superior to traditional lipid membranes, and the hydrogel remains permeable to both ions and most biomolecules, making it ideal for utilization in a sensor system. Additionally, in situ electrical and optical monitoring of the HEMs showed that the gel made intimate contact with the membrane, and that gel formation facilitated membrane self-assembly. Single channels of alpha-hemolysin, were incorporated into HEMs and continuously measured for over 5 days, demonstrating the potential of HEMs for use in stochastic sensing of drug molecules and membrane protein characterization. We will show preliminary data of the application of this system toward the detection of small molecules and DNA as well as the long term stability of the membranes.

COLL 194 Liquid-phase characterization of supported ruthenium catalysts

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Heterogeneous catalysis at solid-liquid interfaces plays an important role in many industrial applications. For example, silica-supported metal (e.g. Ru) catalysts are used in the oxidization of aqueous organic contaminants, water-gas shift of CO to CO_2, Fisher-Tropsch synthesis of alkanes, and fuel cell applications. Although chemical reactions at the solid-liquid interfaces are important in several catalytic processes, few in situ studies have focused on investigating them. Our research efforts focus on using in situ attenuated reflection Fourier transform infrared (ATR-FTIR) spectroscopy to characterize the surface properties of silica-, boehmite-, and NaY zeolite-supported ruthenium (Ru) catalysts in the presence of both gas-phase and liquid-phase water. Specifically, we are studying the adsorption of CO on these catalysts as a function of time, CO concentration, and water concentration. This data will provide information about the nature and concentration of adsorption sites on these catalysts in aqueous environments.

COLL 195 Lubrication of MEMS through vapor phase adsorption of alkanethiols

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Adsorption, adhesion, and contact current studies have been performed on a homologous series of n-alkanethiols and five different fluorinated thiol molecules deposited on Au substrates from the vapor phase. Uptake measurements with a quartz crystal microbalance indicate that short-chain thiol molecules tend to form multilayers. Self-assembled monolayers of fluorinated species tend to be less ordered as the number of fluorine substituents increases. Adhesion and contact current have been measured simultaneously between a Au-coated Si atomic force microscope tip and a Au substrate in the presence of the lubricant vapors. Short-chain n-alkanethiols produced a significant decrease in adhesion and maintained current upon contact up to saturation coverage while their long-chain counterparts precluded current flow upon saturation, even at increased applied loads. More promising results were obtained with fluorinated thiols that demonstrate the potential of such candidates for use as boundary lubricants in gold/gold interfaces by virtue of their film forming properties.

COLL 196 Lyotropic phase behavior of aqueous cationic/maltoside surfactant mixtures and predictive synthesis of ordered mesoporous silica using these surfactants

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Self-assembled nonionic surfactants can be used to create functional adsorption and catalytic sites at the surface of mesoporous sol-gel-derived materials. However, these surfactants typically impart poor long-range order. Improved order and control over the functional site density can be achieved by mixing the nonionic surfactant with a cationic surfactant. As an example, we investigate the lyotropic liquid crystalline phase behavior of aqueous solutions of the functional nonionic surfactant n-dodecyl â-D-maltoside (C12G2) and cetyltrimethylammonium bromide (C16TAB) by polarized optical microscopy. Multiple hydrogen bonding interactions between the DM headgroup and the surface silanol groups of silica should form recognition sites for simple carbohydrates. By replacing the volume of water in the phase diagram with an equivalent volume of silica, ordered mesoporous materials are prepared by nanocasting and dip coating with variable DM:CTAB ratios. X-ray diffraction, transmission electron microscopy, and nitrogen sorption confirm the formation of the predicted phases in most cases.

COLL 197 Metal nanocluster synthesis in polymeric suspensions: Effect of solvent and polymer composition

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In this work we examined the effect of the solvent used in dissolving PS-b-PMMA copolymer and its constituent homopolymers, as well as the effect of the block copolymer relative composition on the ultimate morphology of a metal cluster-polymer nanocomposite. We studied two different cases: (a) Variation of the block copolymer compositions while using a non-preferential solvent for either blocks, and (b) Variation of preferential solvents while keeping block copolymer composition constant. We also studied the effect on metal cluster size when the synthesis was done in the homopolymer versus the copolymer. We found that the spatial distribution of the metal clusters synthesized in-situ coincided with the morphology dictated by thermodynamically-driven microdomain structure of the block copolymer, and that the only parameter (for a fixed copolymer concentration) controlling the cluster size in diblock copolymers suspensions is the MW of one block, PMMA, regardless of the MW of PS or solvent quality.

COLL 198 Micro-textured silicon elastomers by microdroplet patterning for enhanced cell attachment

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A simple method to introduce microstructures to silicone elastomer surface is demonstrated. The patterns are generated by spray-coating a fine mist of protection polymer onto a silicone elastomer film followed by removing the uncoated material by chemical etching. Cell attachment study shows that the fabricated material has a significantly enhanced cellular adhesion compared to its non-treated control.

COLL 199 Microfluidic approach for colloidal chemistry

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Since industry has sought new advances in nanotechnology, developments of new materials and synthesis techniques have been pursued to meet our growing demands in miniaturization. In this talk, we will present design and operation of microfluidic reactors specifically designed for microfluidic synthetic purposes, taking advantage of micro-scale mixing of colloidal reagents and of the use of quenching sequences for greater reaction selectivity. The use of microfluidics offers a number of potential advantages over existing technology. Chemical mixings and reactions run in microfluidic devices have high thermal and mass transfer rates with an opportunity to use more aggressive reaction conditions allowing for improved product yield. Moreover, high chemical homogeneity can be achieved by complex mixing. The microreactors may also be coupled to additional processing steps and in some cases the product may be transported directly for integration into an application device or as part of an assay. The overall goal is to carry out all operations normally performed in a chemical laboratory including synthesis, processing, mixing, purification and analysis on one microfluidic reactors efficiently and economically using minute amounts of solvents and reagents.

COLL 200 Molecular force spectroscopy studies of mPEG assembly with distinct functionalized AFM probes

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AFM molecular force spectroscopy has been used to explore the interaction between poly(ethylene) glycol (mPEG) grafted surface and functionalized probes modified with self-assembled monolayer of distinct terminal group, -CH3, -NH2, -OH, or –COOH. Various types of force profiles were observed in the measurement between the polymer with the functionalized probes. Most force profiles of CH3/PEG interaction demonstrated a JKR model adhesion behavior, whereas those of NH2/PEG, OH/PEG, and COOH/PEG displayed more complicated behavior with distributed probabilities to observe JKR rupture followed by force plateaus, multiple (JKR) ruptures, single JKR rupture and/or none adhesion forms. These results have been correlated to the interfacial energies of the distinct probe/mPEG interfaces and interpreted by polymer dynamics (diffusion at surface and extraction process) at the interfaces. The findings suggest that 1) the microenvironment conditions of tip/substrate can be manipulated by the surface chemical modification, 2) the change of interfacial energies accounts for polymer dynamics (diffusion rate) in the probe surface, consequently change the actual relative tip extension rate to the rate of polymer-surface dissociation/reformation process, and 3) the constant force plateaus are ascribed to the polymer sliding or friction at the probe surface. The force plateaus profiles have been analyzed statistically to obtain the sliding forces and contour length of the polymer with respect to individual functionalized probes, as well.

COLL 201 Molecular layer-by-layer self-assembly of water soluble perylene diimides through g-g and electrostatic interactions

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A layer-by-layer deposition process has been carried out by two oppositely charged perylene diimides without the use of intervening polyelectrolyte layers to form the monolayer assemblies on the substrates. The strong p-p interactions between the perylene moieties help stabilize the layers and simultaneously diminish the fluorescence quantum yield of the array without strongly affecting the absorption or fluorescence spectra. There is an alternation of fluorescence intensity according to which perylene species is on the outer layer, which is interpreted as the effect of facile energy transfer between the perylenes. The extension of this process to the other dye like 1,3,6,8-pyrenetertasulfonic acid tetrasodium salt with the positively charged perylene diimide had been studied.

COLL 202 Multi-scale kinetic model for micelle formation and disintegration

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Dynamics of self-assembly and structural transitions in surfactant systems play an important role in various industrial and biological processes. Although molecular details are crucial for adequate modeling of these processes, the timescales of the processes are typically outside of reach of direct molecular dynamics (MD) simulations. We present development of a multi-scale kinetic model for self-assembly dynamics and apply it to studies of formation and disintegration of spherical micelles. On the molecular scale, the system is modeled by a coarse-grained MD model. On the mesoscopic scale, we use a stochastic model which is based on the assumption that micelle formation (disintegration) takes place by stepwise addition (removal) of single monomers to (from) surfactant aggregates. The rates of the monomer addition and removal are obtained from a series of short-scale MD simulations with a single surfactant molecule constrained within a prescribed distance from the center of mass of a micelle.

COLL 203 Nanotethering of QDs within Laponite/PANI films

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We are currently exploring the nanotethering of organically modified quantum dots (QDs) within Laponite/polyaniline (PANI) films. Aniline tetramers coupled to CdSe quantum dot surfaces using a dithiolate linker were tethered to PANI embedded within the Laponite nanoscaffold. Frequency resonance energy transfer within our tethered QD/PANI/Laponite system were characterized using electronic absorption and fluorescence spectroscopies. The extent of nanotethering and specific host-guest and guest-guest interactions that control nanocomposite photophysical behavior were probed using near-field scanning optical microscopy and infrared spectroscopy. Our studies illustrate that Laponite affords an ideal host framework for the realization of QD based photovoltaics and light emitting diodes.

COLL 204 New capabilities of probing ion adsorption at solid-liquid interfaces with resonant anomalous X-ray reflectivity

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The ability to obtain element-specific information at solid-liquid interfaces is important for studying surface and colloid chemistry. We recently demonstrated the new capabilities of probing geometric and spectroscopic structures of aqueous metal complexes adsorbed at mineral-water interface simultaneously (C.Park et al., 2005, PRL 94, 076104) using Resonant Anomalous X-ray Reflectivity (RAXR). This new technique combines the merits of x-ray reflectivity (e.g., interface-specificity and structural sensitivity) and x-ray absorption spectroscopy (e.g., element-specificity and spectroscopic sensitivity). We demonstrate two new opportunities derived from this method: 1) the determination of model-independent ion distributions at the solid-liquid interface from derived amplitude and phase information of the RAXR spectra; and 2) the use of the RAXR signal to probe ion adsorption isotherms. A fundamental finding from these preliminary observations is that adsorption of multivalent cations is more complex than previously inferred based on classical theories.

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COLL 205 Non-aqueous and aqueous emulsion procedures for conducting polymer nanoparticles

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The synthesis of conducting polymer nanoparticles via a novel non-aqueous emulsion system, consisting of two immiscible organic solvents and a specially designed surface active compound as stabilizer, is presented. The suitability of this system for performing water-sensitive, catalytic, and oxidative polymerizations is demonstrated. Thereby, absolutely spherical nanoparticles such as polyacetylene, poly(3,4-ethylenedioxythiophene) (PEDOT), and poly(thiophene-3yl-acetic acid) with diameters smaller than 35 nm were prepared. After polymerization the stabilizer was removed quantitatively from the particles, and in case of the poly(thiophene-3yl-acetic acid) nanoparticles, the acetic acid group could be used as a functional group for further reactions on the particles surface. In a second approach the aqueous synthesis of PEDOT nanoparticles is presented. Spherical particles with diameters smaller than 40 nm were obtained by using a microemulsion procedure and an ionic surfactant. As the surfactant remains adsorbed on the particle-surface the nanoparticles were able to be redispersed in lower alcohols and processed via ink-jet printing.

COLL 206 Non-steroidal facial amphiphiles

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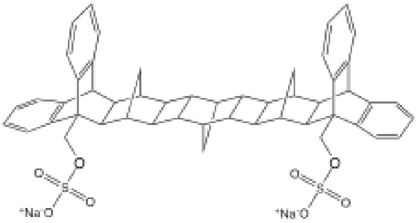
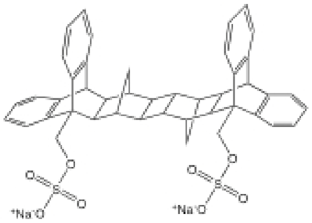
Nature makes wide use of steroidal facial surfactants, such as cholic acid. Chemists have altered these natural substances to create new facial amphiphiles. We now report on the synthesis, characterization, and self-assembly properties of two new anionic amphiphiles that are not steroidal. Surface tension, NMR, and ITC data show that these compounds behave quite differently from conventional linear surfactants.





COLL 207 Novel method for evaluating the deposition of the colloidal resin existing in white-water by rheology tester

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Rheological property of the colloidal resins, which exist in white-water, deposits and seriously lower the runability of paper machine using wood-containing pulp, was investigated here. Various influential variables linking with the viscosity of the colloidal resin was examined using the TA AR2000 rheology tester, as viscosity was the main reason of deposition of resin. Results showed that shear rheology of the colloidal resin exhibited profound differences in response to the changes in temperature or the characteristic of the resin components. Varying the concentration of some components, particularly glycerol trioleate and sterol ester, dramatically changed the shear rheology of the colloidal resin within the temperature scope assayed. The critical concentrations of the above-mentioned components were subsequently obtained by investigating them under the common temperature (50-60°C) of white-water. This research represents a facile and efficient way to further highlight the discipline of resin deposition and better control the deposition in paper machines.

COLL 208 Optimized growth of carbon nanotube arrays

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Carbon nanotubes have great technological potential because of their distinct physical, electrical and thermal properties. A limiting factor in the application of carbon nanotubes is the growth of these structures. Growth is often poor or inconsistent. The goal of this study was to investigate the effects of pressure, humidity and gas flow rates to determine the optimal range of parameters for multi-wall nanotube growth. Growth was conducted using a chemical vapor deposition method. Hydrocarbon gases were thermally decomposed and deposited onto a catalyst. The results of our study yielded a set of conditions where carbon nanotube growth is consistent and provides tall nanotube arrays. The results from the gas flow rate experiments provided insight about the presence of a gaseous growth precursor. This gaseous precursor is the necessary component to be absorbed into the catalyst and initiate growth. These results provide pertinent information about carbon nanotube growth that will aid in their production for future technological applications.

COLL 209 Phase behavior of "overpacked" microgel assemblies

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The colloidal phase behavior of poly(N-isopropylacrylamide) hydrogel microparticles has been investigated using particle tracking and rheometry. We have elucidated the influence of soft colloid “overpacking” on the effective freezing volume fraction (φ_f,eff) of both the crystalline and glassy states. The dependence of the freezing point on the degree of jamming reflects a packing-dependent interaction potential. Furthermore, dramatic differences in the phase behavior for assemblies of particles with varying cross-link density have been observed. This is attributed to differences in surface structure that alter the interactions between assembled particles.

COLL 210 Plasmon resonances of mixed metal nanoparticle assemblies: Coupled linear chains of silver and gold particles

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The effect of interparticle coupling on the plasmon resonances of pairs and sub-wavelength linear chains of metal nanoparticles was investigated using electrodynamic theory. The modeled pairs and chains consisted of identical gold or silver particles or sequences of same sized particles of alternating composition. Interparticle separation and refractive index of the medium controls plasmon coupling- closer spacing and more refractive media leads to stronger coupling. Short chains of identical particles display a single resonance while chains of unlike particles display two resonances, one near each of the uncoupled particle resonances. In the case of on-axis excitation, coupling red shifts the resonances of both like and unlike particle chains. For chains of identical particles increased coupling also leads to resonance enhancement. Among chains composed of alternating gold and silver particles coupling enhances the gold resonance and, in all but the most weakly coupled assemblies, dampens the silver resonance.

COLL 211 Preparation and characterization of a series of new organically modified montmorillonite clays using X-ray diffraction, thermogravimetric analysis and FTIR spectroscopy

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Clays find a wide range of applications, due to their natural abundance and the propensity with which they can be chemically and physically modified to suit great variety of practical technological needs. We have organically modified Sodium Montmorillonite (NaMMT) via ion exchange reactions using a series of alkyl ammonium cations with varying aliphatic chain length from C8 to C20, as well as by certain polar surfactants containing alcohol, carboxyl and aromatic moeties. Some of the organoclays presented here are novel and for the first time. In this complete study, we present validation of correct organic modification and structural details of these organically modified montmorillonites (OMMT) by X-ray diffraction, thermogravimetric studies and FTIR spectroscopy on powder samples. Increase in basal d-spacings by organic modification is in very good agreement with theoretical molecular level calculations. Thermogravimetric analysis shows the amount of surfactant in the exchanged OMMTs in good agreement with theoretically calculated stoichiometric content expected on complete exchange of Na+ ions by organic ions. The OMMTs show stepwise decomposition for organoclays corresponding to degradation due to residual water desorption, dehydration, followed by decomposition of the organic surfactant and the dehydroxylation of the organoclay. FTIR study shows disordered structure of the organic modifiers indicating amorphous packing at the nanoscale. Effect of alkyl chain length and polarity of organic modifiers will be presented in detail.

COLL 212 Preparation and characterization of optically-resonant atomically-flat nanosurface substrates for scanning tunneling microscopy (STM)

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Flat gold nanoparticles (FGNPs) supported on indium tin oxide (ITO) coated glass can be used as optically-resonant atomically-flat substrates for STM studies. We discuss preparation of the FGNPs and a simple method for depositing them on ITO supporting substrates. Characterization with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) shows that FGNPs can be prepared 100–5000 nm across with shapes that range from triangular to hexagonal with thicknesses of 15-25 nm. Converging-beam electron diffraction confirms that the crystallographic orientation of large facet is in {111} direction and the sides are in <110> directions. Single-particle dark-field scattering spectroscopy and UV-vis-NIR spectrophotmetry show the quadrapole plasmon resonance ~800 nm and the dipole plasmon resonance further in the NIR which are size and the shape dependent. The addition of Polyvinylpyrrolidone (PVP) as a stabilizer during growth has a profound effect on the particle morphology, apparently slowing growth in the <110> edge directions.

COLL 213 Preparation and characterization of poly(vinyl acetate)/poly(vinyl alcohol)/clay nanocomposite microspheres

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Novel poly(vinyl acetate) (PVAc)/poly(vinyl alcohol) (PVA)-encapsulated montmorillonite (MMT) clay nanocomposite microspheres with a core/shell structure have been developed via a suspension polymerization approach. In order to prepare the PVAc/MMT and PVAc/PVA/MMT nanocomposite microspheres, which are promising precursor of PVA/MMT nanocomposite microspheres, suspension polymerization of vinyl acetate with organophilic MMT and heterogeneous saponification were conducted. A quaternary ammonium salt, cetyltrimethylammonium bromide, was mixed with the MMT in the monomer phase prior to the suspension polymerization. The incorporation of MMT into the PVAc was verified by FTIR spectroscopy. Organic vinyl acetate monomers were intercalated into the interlayer regions of organophilic clay hosts and followed by suspension polymerization. Partially saponified PVA/MMT nanocomposite microspheres with a core/shell structure were successfully prepared by heterogeneous saponification.

COLL 214 Preparation and characterization of poly(vinyl acetate)/silver nanocomposite microspheres with multi-hollow structure

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High molecular weight poly(vinyl acetate)/silver (PVAc/Ag) nanocomposite microspheres, which are promising precursor of embolic materials, were prepared via a low temperature suspension polymerization in the presence of silver nanoparticles. It was found that a high yield and high molecular weigh poly(vinyl acetate)/Ag could be concurrently obtained even using a low-temperature initiator 2,2'-azobis(2,4-dimethylvaleronitrile). In the case of presence of silver nanoparticles, the rate of polymerization was slightly slower than that without Ag. The suspension polymerization approach introduced could produce PVAc/Ag composite with conversion and viscosity-average molecular weight (Mv) up to 95 % and 1,300,000 respectively, in spite of at low polymerization temperature, in sharp contrast with only ~30% conversion of VAc under bulk polymerization. Morphology studies revealed that except normal suspension microspheres with a smooth surface, a golf-ball-like appearance among the microspheres was observed, due to the migration and aggregating of the hydrophilic Ag nanoparticles at the sublayer beneath the microsphere's surface.

COLL 215 Preparation of liposome templated Germania Nanoshells

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Phospholipids with varying head groups were utilized as templates for the formation of germania nano-shells. The efficiency of shell formation as a function of surface charge, the influence of added organogermanes, and cholesterol was compared. It was found that cationic vesicles were most efficient in the formation of the germania nano-shells, while anionic vesicles were least efficient. The results indicate that germania nano-shells can be synthesized based on the specific interior surface charge of the vesicle templates. Further, we encapsulated various triphenylmethane dyes within the liposome templated germania nanoshells and the photophysical properties of those dyes were studied. Crystal violet and bromocresol green encapsulated in the nanoshells showed enhancement of fluorescnce intensity due to their interaction with the interior of the shell. The methodology presented could potentially be applied to the formation of multidimensionally porous germania with chemically-tailored microcavities for sensor applications.

COLL 216 Preparation of programmed synthesis of anodic aluminum oxide nanopores and corresponding metallic nanowires

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Nanoscience and nanotechnology is one of the most important research fields in modern science. The particles with nanoscale dimensions exhibit properties such as optical, electronic, and chemical reactivity significantly different from bulk materials, and this is of interest from both fundamental and applied viewpoints. Nanoparticles of spherical and cylindrical nanotubes and nanowires can be easily prepared using various well-established methods. Recently, conical nanotubes and nanowires have also been prepared using a template-synthesis method. However, still today more complex shaped nanotubes (bent, tilted, merging, or even hyperbolic) are hard to synthesize. We have synthesized various complex shapes and sizes of high quality gradient nanoporous membranes and nanowires using “programmed” template synthesis. We will further demonstrate programmed gradients of bimetallic nanowires of Ni and Ag metals. We expect that the use of this novel approach will help in advancing, further, the field of nanoscience, and they will find applications in many areas including nanodevices, nanofluidics, biosensing etc.

COLL 217 Preparation of refined gold nanorods: Synthesis, shape separation and optical properties

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In metal nanoparticles science, the optical properties have been of interest especially because of the applications to medical diagnostics and nanooptics. It is important to prepare nanoparticles of well-defined shape and size for properly characterizing the optical properties. Recently there has been growing interest in synthesizing these well-defined nanoparticles using lithographic methods as well as classical wet chemistry techniques by modifying the preparation parameters. We describe improved seed mediated synthesis of gold nanorods producing a high yield of nanorods with low polydispersity. The efficient separation of gold nanorods from mixture of shapes was achieved by understanding the hydrodynamics of nanorods and nanospheres undergoing centrifugation. The optical properties of resulting refined gold nanorods are compared to predictions of existing theories, and the main parameters affecting them such as aspect ratio and the dielectric properties of the environment are discussed.

COLL 218 Probing monolayer stability through chemical reactions on functionalized porous silicon

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Due to its light emission properties and high surface area, porous silicon (por-Si) has shown great potential toward a myriad of applications. While its native hydride-termination is only metastable with respect to surface oxidation under ambient conditions, stability can be enhanced significantly by functionalizing surfaces with organic monolayers. Using thermal, Lewis-acid, and carbocation mediated hydrosilylation methods, we have functionalized por-Si surfaces with 1,7-octadiene, leaving a terminal C=C bond upon which subsequent synthetic transformations can be affected. Conversion of the terminal olefin to a boronic acid via hydroboration provides a gateway to a range of functional groups. We introduce protocols for the synthesis of carboxylic acids and terminal alcohols attainable through boronic acids on monolayers bound to por-Si substrates. These reactions serve as an internal probe for the stability of monolayers bound to por-Si by various fuctionalization methods. Organic transformations and oxidative degradation were monitored via FTIR.

COLL 219 Protein adsorption on hydrophobic regions imbedded in a hydrophilic grafted polymer layer

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Hydrophilic grafted polymer layers containing hydrophobic regions were prepared on the surface of silicon wafer by “grafting to” method. The polymers were anchored to the substrate via poly(glycidyl methacrylate) anchoring layer. First, carboxy terminated poly(ethylene glycol) (PEG) was grafted to the modified silicon surface followed by the grafting of the polyacrylic acid–b-polystyrene (PAA-b-PS) diblock copolymer. Polystyrene blocks of the copolymer formed hydrophobic (protein attractive) regions distributed in PEG/PAA hydrophilic (protein repelling) layer. Treatment of the layer with different solvents changed surface morphology of the polymer assembly. Specifically, the hydrophobic regions were hidden under layer of PEG/PAA when good solvents for the hydrophilic polymers were used. Adsorption of fibrinogen from phosphate buffer on the surface of the layers treated with the solvents was studied.

COLL 220 Protein immobilization on activated SAM nanopatterns produced by nanografting

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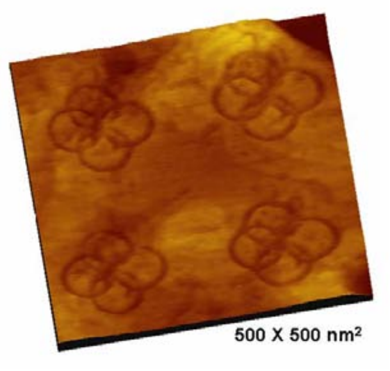
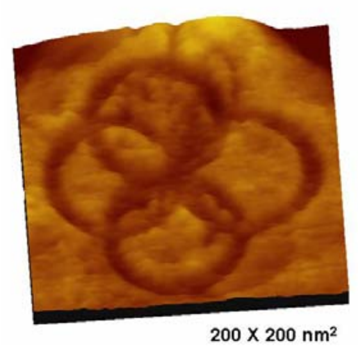
Using computer programs, an AFM tip can be rapidly and uniformly translated at designated speed, direction, and force to enable reproducible fabrication of arrays of nanopatterns with well-defined shapes and sizes. Automated nanografting is applied to fabricate regular arrays of nanopatterns (10-300 nm) of n-alkanethiol self-assembled monolayers (SAMs) with designated terminal chemistries. The surface groups (carboxylate or aldehyde) of SAM nanostructures are chosen for binding model proteins through electrostatic interactions or are chemically activated using NHS and EDC for covalent immobilization. AFM topographs of example nanostructures are shown for rings of 11-

mercaptoundecanoic acid inscribed within an octadecanethiol SAM. Height changes are used to monitor successive surface changes with protein adsorption during in situ experiments. Nanografting provides superb control of parameters such as the ligand density, pattern spacing and sizes/shapes of array elements. In situ experiments furnish information regarding protein orientation and the selectivity and efficiency of SAMs for binding biomolecules to surfaces.





COLL 221 Protonation-induced lyotropic liquid crystal assembly of cross-linkable monomers containing protein anti-fouling functional groups

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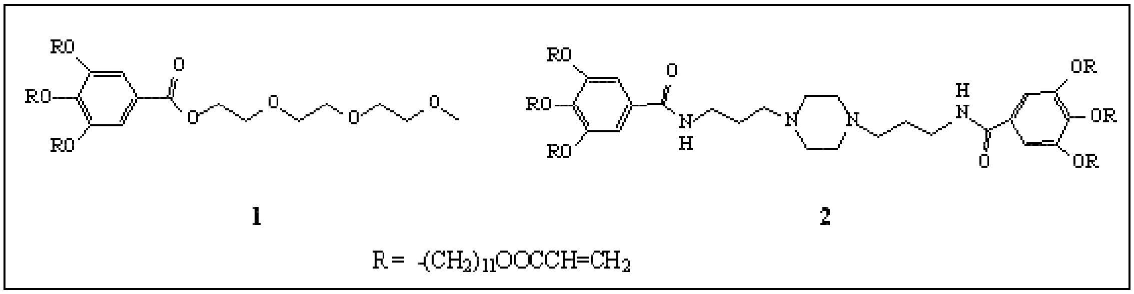
Research in our group is focused on the design, synthesis and characterization of functional nanostructured materials via self-organization and polymerization of lyotropic liquid crystal (LLC) monomers. The goal of this particular project is to prepare nanostructured polymer materials containing protein anti-fouling groups, in order to determine the roles of surface chemistry and nanostructure on protein adsorption. This poster will present the preparation and characterization of two novel cross-linkable LLC analogs, **1** and **2**, containing organic groups known to have excellent protein anti-fouling properties. Monomers **1** and **2** are neutral and non-mesogenic, but protonation of **1** and **2** with H_2SO_4 was found to induce LLC self-assembly in water. Free-standing films of poly-**1** and poly-**2** were successfully prepared via radically initialized polymerization. Polarized optical microscopy and X-ray was used for the determination of the LLC nanostructure.



1 **2**

R = $-(CH_2)_{11}OOCCH{=}CH_2$

COLL 222 Purification and reconstitution of Maxi-K ion channels into artificial membranes

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Ion channels mediate the flow of ions across biological membranes. Their activity can be monitored by carrying out electrophysiological studies using patch clamp techniques. We have isolated Maxi-K, a voltage-gated K+ channel from its natural expression system,the *Xenopus laevis* oocyte membrane, incorporated in lipid vesicles, reconstituted in an artificial bilayer lipid membrane and then measured single channel activity upon the application of electrical potential across it. Since it is isolated from oocyte membranes, during reconstitution Maxi-K comes along with pre-membranal material, natural lipids, proteins and other membrane components which may perturb or mask the Maxi-K channel activity. We have developed a chromatographic purification protocol which should help to enhance signal quality as well as provide better control and reproducibility of electrophysiological results. Preliminary investigations show viability of the ion channel after the purification procedure demonstrated by signals obtained indicating opening and closing events.

COLL 223 Quantitation of nonspecific adsorption on SAM biosensor platforms using immunoassay techniques

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Abstract:

Non-specific adsorption of immunoactive compounds on biosensor surfaces is an important concern in biosensor development. In this study, minimization of non-specific adsorption onto self- assembled monolayer (SAM) biosensor platforms was studied using electrochemical immunoassay techniques.

To compare non-specific adsorption resistance, Au electrodes individually modified with decanethiol (DT), tetraethylene glycol thiol (EG4-SH) and 11-mercapto-1-undecanol (11-MUD) monolayers were compared to two component mixed monolayers based on these compounds. The compositions of mixed SAMS were determined by Raman spectroscopy and reflection-adsorption infrared spectroscopy (RAIRS). The electrochemical immunoassay experiments showed that the tetraethylene glycol thiol was the most resistant to non-specific adsorption.

COLL 224 Quantum dots synthesis and energy transfer through DNA

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Abstract: Semiconductor quantum dots (QDs) synthesis and DNA-CdSe assemblies are of substantial significance to the nano-materials research. An interesting and perplexing detail of the CdSe NC system is the ubiquitous use of tri-n-octylphosphine oxide (TOPO) as a coordinating ligand to cap the growing nanocrystals. The replacement of TOPO is very important for explaining the precise function of TOPO in the preparation of CdSe NCs, for developing greener methods for producing CdSe NCs, and for producing high quality CdSe NCs in aqueous solution. We discovered that TOPO can be replaced by weakly coordinating molecules such as hexadecyl hexadecanoate (HH) or benzophenone (BP). Using this new method, high-quality CdSe and core/shell CdSe/ZnSe/ZnS nanocrystals were synthesized without the need for post-preparative size selection. DNA is an ideal synthon for programming the assembly of nanoscale building blocks into two- and three-dimensional extended structures. We are using DNA oligomers as fixed-length, rigid linkers to bind CdSe/ZnSe/Zns particles into multi-QD assemblies for the purposes of studying electronic interactions between the individual QDs. The transfer of electronic excited state energy between QDs can thus be studied in detail for the first time. This excited state energy transfer may have implications for novel solar energy conversion devices, information processing systems, and QD laser pumping.

COLL 225 Quasielastic neutron scattering study of the dynamics of 1,3-diphenylpropane grafted to the pore surface of MCM-41

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An initial study of the dynamics of 1,3-diphenylpropane (DPP, $\equiv Si\text{-}O\text{-}C_6H_4(CH_2)_3C_6H_5$) attached to the surface of the mesoporous silica MCM-41 has been carried out using quasielastic neutron scattering. Measurements of the elastic intensity were carried out in the temperature range 50-380 K and indicate a trend in DPP dynamics with changing grafting density and pore size. Full quasielastic scans over an energy range of ± 17 μeV were carried out at temperatures of 240 K, 280 K, and 320 K. Initial analysis employed a stretched exponential to model the Fourier transformed data in the time domain. An average relaxation time, defined as $\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta)$ where β is the stretched exponent in the model, shows a dependence on temperature, pore size, and DPP grafting density. Molecular dynamics simulations using a model for DPP grafted onto the surface of MCM-41 was compared with the experimental results.

COLL 226 Radiation sensitive liposomes

Bruce Bondurant[1], Bob Sutherland[2], Christopher J. Bondurant[1], and Mark W. Dewhirst[3]. (1) Department of Radiation Oncology, Duke University Medical Center, 295 MSRB, Research Drive, Durham, NC 27710, Fax: 919-684-8718, bruce.bondurant@duke.edu, (2) Varian Biosynergy, (3) Radiation Oncology, Duke University Medical Center

We have developed a liposome formulation containing polymerizable bis-Sorbyl lipids which, when exposed to gamma radiation releases contents at a 10 fold higher rate than for non-irradiated liposomes. Liposomes composed of DAPC and a polymerizable lipid having two sorbyl ester bearing fatty acid chains were found to leak only 6% of an encapsulated fluorescent dye after 1.5 hr at 37¢ªC. When exposed to 20 or 50 Gy of gamma radiation, these liposomes were found to release 70% or 90% of contents, respectively during the same time period. This enhanced leakage occurred in conjunction with a 20% to 30% loss of monomer, as measured by a decrease in absorbance at 250 nm.

COLL 227 Role of C60-modified PVK film on the device performance of polymer bistable device

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A nonvolatile organic memory was fabricated by utilizing polyvinyl carbazole (PVK) and fullerene (C60) as an electron donor and acceptor, respectively. The bistable characteristics of PBD have mainly been impeded by ununiformity of electron acceptor materials in PVK, which has been a bottleneck from scientific and technological point of view. PVK was chemically modified with C60 via nucleophilic reaction of polymeric carbanions generated from organometallic reagents to obtain the homogeneous distribution of C60 in the PVK molecule. The device was fabricated with a simple structure consisting of the PVK and C60 film sandwiched in between two Al electrodes. The current-voltage characteristics of semiconducting film of C60-modified PVK were compared with that of PVK doped with C60 via liquid phase mixing. The device with C60-modified PVK showed dramatically increased bi-stability (Ion/Ioff ratio) for PBD and good repeatability.

COLL 228 Self assembled growth of Au nanocrystals on CdS nanorods

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Nanorods of S^{2-} rich CdS with ~15 nm in diameter and ~80 nm in length were synthesized by reaction of excess S versus Cd precursors in the presence of ethylene diamine. The photoluminescence (PL) emission from the S^{2-} rich CdS nanorods was broad with a peak at ~710 nm, which was 40 nm longer in wavelength than the PL peak from Cd^{2+} rich CdS (~670 nm) nanorods. The influence of surface electron or hole trap states on the luminescent pathway of CdS nanorods will be discussed to explain these shifts in wavelength. Nanocrystals of Au with ~2 nm in size were grown on S^{2-} rich surfaces of CdS nanorods. Significant luminescence quenching was observed from Au nanocrystals on CdS nanorods due to interfacial charge separation. Charge separation by Au nanocrystals on CdS resulted in enhanced photocatalytic degradation of Procion red mix-5B (PRB) dye in aqueous solution under UV light irradiation.

COLL 229 Self-adhesion among phospholipid vesicles

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Abstract. A compound was synthesized that binds to a phospholipid bilayer via a hydrophobic steroid thereby projecting a strong multi-hydrogen bonding unit into the surrounding water. As shown by light scattering, light microscopy, and cryo-HRSEM, this latter unit self-adheres, and induces membrane-membrane attachments, as found in many biological systems.

COLL 230 Self-assembled chemical gradient on gold films with nanostructured topography

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Chemical gradients are keys to a variety of biological processes and novel phenomena including axonal guidance for neuron regeneration and making water run uphill. In this poster, we describe the design and fabrication of a self-assembled chemical gradient that allows the control of a uniform structure and presentation of each functional group in the chemical gradient. By vapor deposition of gold atoms at an increasing incident angles on a glass, a gradient in the thin film structure and properties are obtained, including particularly the polycrystallinity and the surface area of the nanotopography. When supporting self-assembled monolayers of alkanethiols, the surface density of alkanethiols doubles across the gradient nanotopography while retaining the well-packed structure of the monolayer. We will present the quantification of this chemical gradient as well as the control of mammalian cell adhesion and confinement on this gradient.

COLL 231 Self-assembly and bonding of nanowire assemblies using adhesive and solder

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One promising nanomanufacturing strategy is to direct the assembly of nanoscale components from the bottom-up. The nanocomponents are engineered so that they are capable of interacting with one another, to form organized integrated structures. Several interaction forces have been used to direct assembly of nanocomponents including the use of molecular recognition, electrostatic forces, dielectrophoresis, magnetic forces, or surface tension based forces.

We demonstrated the fabrication of 2D and 3D structures composed of nanowires that were bonded to each other and to substrates using a curable adhesive or solder. In our strategy, liquid interfacial layers of an organic adhesive or molten solder on specific regions of the nanowire facilitated binding between components by minimization of interfacial free energy (surface tension driven self-assembly). The adhesive and solder were subsequently hardened by curing (polymerization) and cooling respectively. In the case of the adhesive, the 2D and 3D structures formed survived mild sonication and could be taken out of the fluidic medium without disruption. In the case of solder it was possible to form ohmic low resistance contacts that points to the feasibility of using these joints as nanoscale electrical contacts.

COLL 232 Self-assembly of bionanoparticles at liquid/liquid interface

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The self-assembly of nanoscale materials to form hierarchically ordered structures promises new opportunities in optical, acoustic, electronic, as well as magnetic materials and devices. We investigated the self-assembly of bionanoparticles (BNPs) at liquid/liquid interface to form two-dimensional ordered arrays. Spherical particles, wild type cowpea mosaic virus and turnip yellow mosaic virus, were both employed to assemble at aqueous/oil interface, which led to ordered hexagonal arrays in an area of tens of square microns. Rod-like tobacco mosaic virus was also used in our study, and closely packed parallel arrays have been generated at the aqueous/oil interface. In all the situations, single BNP layers have been observed. We have evaluated the impacts of the concentration of viruses and crystallization reagents as well as the ionic strength and density of the solution on this self-assembly process. TEM, AFM, SEM, and other scattering methods have been employed to analyze the assembled arrays.

COLL 233 Simulation of Brownian particle deposition in porous media by applying the triangular network model using the Brownian dynamics simulation method

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The effects of different interaction energy curves of DLVO theory and the wall geometry of the constricted tube model on the permeability reduction in a filter bed is investigated by applying the triangular network model using the Brownian dynamics simulation method, when the movement of individual Brownian particles through the porous media is considered. When energy barrier exists and both the particle and the pore size distributions are of the Raleigh type, it is found that the particle collection efficiency is strongly dependent on the geometry of the tube and on the shape of the total interaction energy curve. It is found that the present model shows fair agreement between the theory and the filter coefficient experimental results when the direct deposition mechanism is dominant.

COLL 234 Size dependence emission quenching properties of dye capped gold nanoparticles

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Particles with sizes in the range of 1-100 nm have been demonstrated to exhibit size dependant physical properties that differ from bulk materials. Here we present results on dye fluorescence quenching induced by gold nanoparticles having different sizes. Gold nanoparticles strongly quench the singlet-excited states of chromophores when it adsorbed on nanoparticle surfaces, through an energy-transfer mechanism. Fluorescence spectra clearly show that the quenching efficiency decreases with decreasing size of the gold nanoparticles and increasing the distance between dye anf nanoparticles. This suggests that the quenching is a result of electron transfer rather than long-range (Forster-type) energy transfer processes. The quenching was attributed to the transfer of electron with energies below the Fermi level of gold.

COLL 235 Statistical thermodynamics of DMPC/DHPC "bicelle" mixtures

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Mixtures of DMPC and DHPC lipids contain aggregates with a variety of morphologies. To a first approximation, these aggregates can be decomposed into two-dimensional bilayer regions rich in DMPC lipids, bounded by one-dimensional edge regions rich in DHPC. On top of the system's composition and total lipid concentration, other effects play a role in determining the equilibrium distribution of aggregates. These include translational/rotational entropy, surface/edge bending energy, excluded volume effects, and the entropy associated with the fluctuations of the surface and the edge. Using simple free energy models that take these effects into account, we study the coexistence of various morphologies including disks, ribbons, perforated lammellae, and perforated vesicles.

COLL 236 Structural effects of cross-linking a biopolymer hydrogel derived from a marine mussel protein

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The structure of a biopolymer hydrogel is studied by microscopy, scattering and rheology. The starting gel is found to have a porous structure on length scales detected by Scanning Electron Microscopy and optical microscopy. "Disorder" is observed on length scales smaller than a few microns. Cross-linking with iron condensed the gel structure on a micrometer level. On length scales smaller than a few microns the "disorder" remains. Partial cross-linking transformed the viscoelastic starting gel into one with more rigid and elastic properties. Overall, the preliminary results on the elasticity, porosity, and biological origin of this protein-based hydrogel makes it a promising candidate for biomedical applications where disorder or porosity can be used as structural design component.

COLL 237 Study of the phase transition behavior of self-oscillating PNIPAM particles

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A self-oscillating gel was synthesized via copolymerizaion of N-isopropylacrylamide (NIPAM) and a Ru catalyst crosslinker. In the presence of substrates of the Belousov-Zhabotinsky (BZ) reaction, the size of the gel particles oscillates due to the periodic change in polymer hydrophilicity induced by the chemical oscillation. We report here the preparation of particles of relative uniform size and the study of their phase behavior by use of UV-Vis spectroscopy and light scattering techniques.

COLL 238 Supramolecular structures in nanocomposite multilayered films made from solutions

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We investigate the multilayered structures of PEO/Montmorillonite nanocomposite films made from solution. In solution the clay particles are exfoliated and act as multifunctional cross-links to the polymer building a network. The shear orientation of this network combined with the simultaneous solvent evaporation leads to supramolecular multilayer formation. The resulting films have highly ordered structures with sheet-like multilayers on and blob-like chains on the nanometer and micrometer length scales. Inside the blobs, small angle scattering experiments indicate the polymer covered and stacked clay platelets orient in the plane of the film. The polymer is partially crystalline although this is not visible by optical microscopy. The nanocomposite films studied here show re-intercalation of clay platelets in films made from exfoliated polymer-clay solutions as well as the supramolecular order and hierarchical structuring.

COLL 239 Surface chemistry of $Ti_{0.3}V_{0.6}C$ with CO and ethanol

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Fundamental studies of the surface reactions of single crystal mixed metal carbide $Ti_{0.3}V_{0.6}C$ (100) with carbon monoxide (CO) and ethanol have been performed and compared with that of TiC (100) and VC (100). Valence band XPS of the three carbides shows additional 3d peak intensity at 0.5 eV on both VC and $Ti_{0.3}V_{0.6}C$ but not on TiC. Temperature programmed desorption measurements have documented the relative desorption temperatures of CO from the three carbides (VC > $Ti_{0.3}V_{0.6}C$ > TiC). High resolution electron energy loss spectroscopy of CO on mixed carbide indentified a lower C-O stretching frequency observed on $Ti_{0.3}V_{0.6}C$ as compared to $2120cm^{-1}$ on TiC, indicative of π-backbonding mechanism and consistent with the TPD and valence band data. The TPD of ethanol on $Ti_{0.3}V_{0.6}C$ showed similar desorption profiles with that of VC and reactivity intermediate to VC and TiC.

COLL 240 Surface modification of biomaterials via photochemical immobilization for small diameter vascular grafts

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Surface modification of biomaterials via aryl azide photochemical method represents a powerful approach towards ultimate anti-thrombogenic small diameter vascular grafts. A new synthesis of methyl 4-(2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethylcarbamoyl)-2-(diphenylphosphino) benzoate will be reported. The PEGylated aryl azide compound with amine end groups can be chemically immobilized onto medical grade poly(ether urethane) thin film under UV irradiation. The resulting amine group surface grafting density ranges from 4.85 to 14.32 $nmol/cm^2$. This provides a diverse platform for introducing bioactive molecules onto the surface.

COLL 241 Surface modification of PET and Nylon films with polymer grafting

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The study is focused on modification of poly(ethylene terephthalate) PET and Nylon-6 films using "grafting to" approach. Reactive anchoring interface was created by deposition of poly(glycidyl methacrylate) ultrathin layer on the surface of the films. Functional hydrophobic and hydrophilic polymers were grafted to the surface employing the macromolecular anchoring layer. Atomic Force Microscopy (AFM) technique and contact angle measurements have been applied to characterize the surface morphology and wettability of the modified films.

COLL 242 Surface modification of Tobacco Mosaic Virus using “click” chemistry

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Development of new bioconjugation chemistry to functionalize nanoparticles is pivotal for many applications, including targeted drug delivery, electronics, and sensing. It is highly demanding to develop new chemistry which is compatible to biological scaffolds with high reaction efficiency. We employed the 1,3-dipolar cycloaddition reaction of azides and alkynes, known as “click” chemistry, to chemically modify tobacco mosaic virus (TMV). Acetylene groups can be anchored on the surface of TMV via the tyrosine residues, which is sequentially reacted with azides. The functionalized viral particles retain their integrity after the reaction as evidenced by TEM and size exclusion chromatographic analysis. Furthermore, fluorescent tags are utilized to quantify the reaction efficiency, and MALDI-TOF MS is employed to determine regio- and chemo-selectivity of these reactions.

COLL 243 Surface photochemistry of heteropoly tungstates in nonpolar solvents

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A broad absorbance peak centered at 656nm appears in the UV/Vis spectrum of the keggin-type SiW11NiO39(6-) anion, when it is irradiated with broadband UV light. This absorbance corresponds to a reduction of the SiW11NiO39 anion. This reduction is a result of electrons being transfered from ethanol, that is coordinated to the Ni. This reactions works in neat ethanol, and in solutions of toluene and ethanol and in aqueous ethanol. This indicates that hydrogen bonding or intermolecular interactions are needed to stabilize the ethanol-SiW11NiO39 complex. The blue color fades when CO2 is bubbled through the reduced SiW11NiO39 in toluene and in neat ethanol. No color change is observed when CO2 is bubbled through the reduced SiW11NiO39 in aqueous ethanol.

COLL 244 Surface treatment and characterization techniques for lowering dust adhesion to Mars calibration targets

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Correct interpretation and radiometric modeling of images received from the Panoramic Camera, on board Mars Exploration Rover relies on precise color calibration. An imperative property of the calibration targets is that their surfaces must follow Lambert's Cosine law of reflection. This translates into surface heterogeneities that can act as trapping sites for the micrometer-size dust particles present in Mars atmosphere, caused by frequent dust storms. The tacky nature of the polymer that is currently in use adds to the dust entrapment problem. Therefore, significant degradation of optical resolution is observed. However, properties of this polymer e.g. toughness, flexibility, low outgassing, and wide range temperature stability are superior to other materials available. Our approach towards eliminating these problems has been to maintain the original design structure yet apply non-invasive thin film technology consisting of a polymer-metal sandwich structure that would create a smooth and transparent finish with inert chemical properties.

COLL 245 Synthesis and characterization of perfluorinated gold nanoparticles

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A new kind of perfluorinated gold nanoparticle is synthesized using ligand exchange reaction of Au55(PPh3)12Cl6 with pentafluorobenzenethiol. The exchange product is found to have the formula Au75(SC6F5)31 by Mass spectrum, TGA and NMR. This perfluorinated nanoparticle is soluble in organic solvents such as CH2Cl2, toluene,etc, while insoluble in fluorous solvents or liquid CO2. Square wave voltammogram shows an electrochemical gap ~ 740 mV similar to Au75(SC6)40. However, TEM and HPLC results show that it is more polydisperse than Au75(SC6)40.

COLL 246 Synthesis and characterization of switchable, bio-compatible aggregates based on caged ferrocenyl amphiphiles

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We report the design, synthesis and characterization of redox active amphiphilies, where a ferrocenyl group is covalently linked and complexed in the annular void of a cyclic oligosaccharide, b-cyclodextrin (bCD). The instability of the oxidation state of ferrocene – ferrocenium ion – in the present of weak nucleophile such as simple chloride ions prevents its good utility in biological buffers. By covalently attaching an aliphatic ferrocene to a bCD, we achieved an novel amphiphile that is stable in biological buffers such as cell culture medium. Employing a wide range of characterization techniques such as 2-dimensional NMR spectroscopy, circular dichroism, electrochemistry and dynamic light scattering, we characterize the inclusion complex between ferrocenyl group and bCD, and its low critical aggregation concentration in water. We further demonstrate that the folding of a membrane protein is stable in the presence of aggregates formed by this amphiphile.

COLL 247 Synthesis and optical properties of shape-controlled europium-doped Gadolinium Oxide nanocrystals

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Shape-controlled europium-doped gadolinium oxide (Gd_2O_3:Eu) nanocrystals have been synthesized by a high temperature solution phase method. Thermal decomposition of Gd acetate in the presence of trioctylphosphine oxide (TOPO), oleic acid, and benzyl ether leads to highly crystalline, monodispersed plate-type Gd_2O_3:Eu nanocrystals with an edge length of 5 nm and a platelet thickness of 1 nm. Upon drying a hexane colloidal solution, stacks of plate-type Gd_2O_3:Eu nanocrystals were self-assembled in parallel lying on their edge. Alternatively, reaction of $Gd(acac)_3$ with hexadecanediol results in sphere-type Gd_2O_3:Eu nanocrystals with a diameter of 2 nm, indicating the type of metal precursors plays an important role in controlling the shape of the nanocrystals. The effects on crystal growth of other reaction parameters, such as reaction temperature and combinations of organic solvents, will be discussed. Europium-doped Gd_2O_3 nanocrystals exhibit the characteristic Eu^{3+} photoluminescence emission lines. The effects of the shape and size of the Gd_2O_3:Eu nanocrystals on their luminescent properties will also be reported.

COLL 248 Synthesis and polymerization of diacetylenethiol-functionalized gold nanoparticles

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We are interested in the assembly and manipulation of nanoparticles that incorporate the diacetylene moiety in the thiol capping agent. Octadecanethiol- and heptadecadiynethiol-capped gold nanoparticles were prepared in two different sizes. Thermal analysis of the diacetylene functionalized gold nanoparticles revealed a sharp mass loss event followed by a much slower, ill-defined event, while the octadecanethiol-functionalized gold nanoparticles showed only a single, large event. The nanoparticles were irradiated under UV light while dissolved in various solvents or when in the solid state. The UV-visible spectra for the diacetylene-functionalized nanoparticles showed a significant shift in the frequency and intensity of the plasmon absorption peak, while the spectra for the alkanethiol-functionalized nanoparticle indicated, as expected, very little or no change. The differences in behavior will be discussed in terms of the topotactic photopolymerization reaction of highly organized diacetylenes. Intercalation of octadecadiynoic acid with both sets of nanoparticles was carried out in THF, and the intercalated nanoparticles were irradiated 1.5hr and then studied using NMR, IR, and Raman spectroscopies.

COLL 249 Synthesis and properties of novel, asymmetric hybrid nanoparticles

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Materials on the nano- scale attract considerable interest because of their unusual properties and potential for novel, practical applications. Activity in this field over the last decade has led to remarkable achievements, primarily in the synthesis of homogeneous 1-200 nm nanoparticles of various metals, metal oxides, semiconductors, and polymers. It is well recognized however that the properties of nanoparticles can be further extended if they are incorporated into hybrid structures. Here a novel method for creating such structures is proposed by depositing caps of different types of materials on the surface of otherwise homogeneous nanoparticles. Such asymmetric hybrid nanoparticles (AHNs) will exhibit combined properties of both the core and caps as well as novel properties due to core/cap and cap/cap interactions. The multifunctionality of these particles can be expanded simply by the integration of various optical, electric, magnetic, and chemical properties through a relatively simple deposition process.

COLL 250 Synthesis of aggregation-resistant gold nanoparticles

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A solution of gold nanoparticles, prepared by citrate reduction, flocculates when the ionic strength reaches 0.1 M or in the presence of oppositely charged macromolecules. Since many of the proposed applications of gold colloids include targeted delivery of therapeutic or diagnostic agents to a cell of interest, there is a need to produce nanoscale shuttles capable of surviving the stringent in vivo environment. Ligand exchange reactions were utilized in the production of aggregation-resistant gold nanoparticles, having an average diameter of 5 nm, comprising a gold core capped with a mixed shell of citrate and zwitterionic ligands. As evidenced from UV-Vis absorption spectroscopy, the prepared nanoparticles were stable in saline media with salt concentrations as high as 3.0 M. Similarly, the gold nanoparticles did not precipitate out of solution when positively charged polyelectrolytes, or biopolymers were added, indicating the absence of non-specific interactions. Methods to synthesize the zwitterion capping ligands are also provided.

COLL 251 Synthesis of catecholic amphiphiles for TiO2 surface modification

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The catecholic amino acid DOPA (3,4-dihydroxyphenylalanine) is present in high concentrations in mussel adhesive proteins, which are responsible for strong adhesion of marine mussels to a range of substrates underwater. We are interested in exploiting the known adhesive properties of DOPA for surface modification. Our previous studies focused on modification of TiO2 and other surfaces with DOPA-containing polymers such as poly(ethylene glycol) (PEG). DOPA proved to be a robust and versatile functional group for anchoring polymers onto surfaces for purposes of minimizing fouling by proteins and cells. In this paper we report our preliminary attempts to synthesize and characterize DOPA and related dopamine surfactant molecules. In that regard, mono-alkyl and di-alkyl DOPA and dopamine derivatives were synthesized with varying chain length from C12 to C18. The ability of these amphiphilic molecules to form self-assembled monolayers on TiO2 surfaces was assessed by contact angle goniometry, ellipsometry and XPS.

COLL 252 Tailoring the chemical functionality of liquid crystals to control their anchoring on chemically functionalized organic surfaces

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We report two methods that permit manipulation of the anchoring of 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal on various chemically functionalized organic surfaces. The methods rely on manipulation of the chemical functionality present in the liquid crystal. The first method involves the direct addition of an acid dopant, 4-cyano-4'-biphenylcarboxylic acid, to 5CB. The second method involves exposure of the liquid crystal to UV light to introduce 4-cyano-4'-biphenylcarboxylic acid and other oxygen containing products into the liquid crystal. Both methods were shown to promote homeotropic orientations on ammonium-terminated surfaces. The orientational transition of the UV-treated 5CB was dependent on the thickness of the film of liquid crystal, consistent with the influence of an electrical double layer on the orientation of the liquid crystal. Homeotropic orientations were also promoted on hydroxyl-terminated surfaces, but on these surfaces the orientation of the liquid crystal was not dependent on the thickness of the film of liquid crystal suggesting that the mechanism leading to homeotropic alignment involves a short-range interaction with the surface (e.g., hydrogen bonding). In contrast, the orientational behavior of the 5CB on methyl-terminated surfaces was not influenced by the introduction of the acid functionality into the liquid crystal. These results illustrate how the chemical functionality of liquid crystals can be exploited to tune the orientations of liquid crystals at chemically functionalized surfaces. This poster will illustrate the utility of these methods by tailoring the orientational behavior of liquid crystals at surfaces to report the presence of proteins patterned on surfaces.

COLL 253 The formation of SDS micelles modeled using static light scattering under different flow conditions

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In observing the micellization process using static light scattering we have observed a phenomenon near the CMC. This has been seen for several different surfactants. This work looks in detail at the development of the SDS micelle under different flow conditions to verify that it is in fact a real phenomenon. A model is presented here to describe the process of the development of micelles as they go form individual molecules to their unique aggregates. The sizes of the micelles or aggregation number often vary but the concentration at which the micelles have formed is well known (CMC). This work provides an explanation for this occurrence. Although this molecule has

been studied thoroughly it has not been explored in the region below the CMC nor have there been many models explaining the variation in the aggregation number.

COLL 254 The photophysics of doxorubicin in poly(N-isopropylacrylamide) microgels

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Doxorubicin (DX) has been widely used in cancer chemotherapy. However, the drug has also proven to display broad spectrum cytotoxicity, cardiotoxicity, and is also a target of multidrug resistant cancers. Accordingly, many groups have explored methods for the encapsulation and directed delivery of the drug in order to mediate these side effects. In this contribution, we describe fundamental photophysical studies of DX dynamics in poly N-isopropylacrylamide-co-acrylic acid microgels. Using steady state fluorescence, emission anisotropy, and time-resolved emission, we show DX to be a very environment-sensitive chromophore. For example, at the phase transition temperature of the microgels, the DX fluorescence anisotropy (r) displays a dramatic decrease to a value that is lower than that of DX in water. In the transient fluorescence, the lifetime shows a sudden increase at the lower critical solution temperature of the microgel. These two observations arise from the formation of dimers or aggregates in the microgel during the polymer phase separation event. These results, in addition to steady-state measurements of vibronic peak ratios provide better understandings for the encapsulation environments of DX in thermoresponsive microgels.

COLL 255 The role of cell geometry on free convective flow of non-Newtonian fluid using the Power Law model

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From a large variety of colloidal fluids, those presenting pseudo-plastic and dilatants properties have capture de attention of developers in search of new chemical products and its potential uses. The implications in terms of understanding the most basic unit operation and transport phenomena are not simple. Although the hydrodynamic developed by non- Newtonian fluids and induced by pressure driven forces has been study in the past, the influence of other forces has not been fully engaged. One avenue commonly used to assess the divergent Newtonian behavior has been the Ostwald-de Waele Model “Power Law Model” directly related to the velocity field of the fluid.

This contribution focuses on the study of the hydrodynamics triggered by free convective forces, i.e. thermal effects on different non-Newtonian fluids in different type of cell geometry. Further more, the comparison of results using rectangular and cylindrical geometries cells are presented. Several cases of Joule heating generation are examined and their implication to electrophoretic-type applications analyzed. The analysis uses a novel solution approach that allow to apriori identify the region of possible flows regimes and, therefore, captures the whole range of steady-state solutions that, otherwise, maybe missed.

COLL 256 Thermally and photochemically cleavable surfactants

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Although surfactants are used in minute quantities, they are nonetheless critical to many industries. Unfortunately, their strength is also their weakness because they are difficult to dispose of and result in emulsions that are undesirably stable. Several cleavable surfactants have been designed with a “built-in” group that will allow the surface active character to be switched off. Such abilities will tremendously change the use and disposal of surfactants to the benefit of industries, customers, and environment. We have designed cleavable surfactants that with a “switch” will break into a hydrocarbon molecule and a gas molecule. In addition, these molecules have little or no water solubility or can be easily remove from aqueous stream. We report the synthesis, characterization and cleavability of novel surfactants containing thermal and photochemical switches. The results demonstrate their potential for chemical processes and beyond.

COLL 257 Thioacetate functionalized metal complexes and optical molecular switches: Precursors for Self Assembled Monolayers (SAMs) on gold

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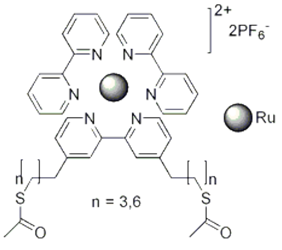
Ruthenium(II)trisbipyridine complexes **1** containing two mercapto-alkyl chains [1] on one of the bipyridyl units have been self assembled on gold and the electrochemical and photophysical properties, thereof, investigated. In the field of sensors, such strong emitting metal complexes can be used for the detection of extremely small quantities of oxygen. The syntheses and photoisomerisation of a thioacetate functionalised, perfluorodithienylcyclopentene [2] based molecular switch **2** has been realized successfully. The immobilisation of this di-thioacetate moiety between gold electrodes is underway to study possible applications in the fields of data storage and molecular level logic gates.

The authors thank GROWTH project [G5RD-CT-2002-00776-MWFM] for financial support.

[1] a) J.-C. Chambron, J.-P. Sauvage, *Tetrahedron* **1987**, 43, 895-904. b) V. M. Iyer, H. Stoeckli-Evans, A. D'Aleo, L. De Cola, P. Belser, *Acta Cryst. C* **2005**, C61, o259-o261.

[2] A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake, M. Irie, *J. Org. Chem.* **2001**, 66, 3913-3923.



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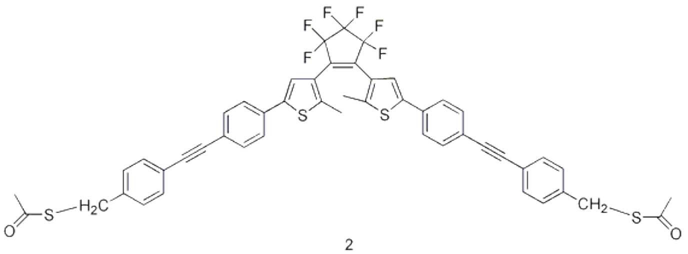

2

COLL 258 Topology of the electron density and nature of organic/metal interfacial interactions

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In our previous study (P.M. Mitrasinovic, Can. J. Chem. vol. 81, pp. 542-554, 2003), the quantum theory of atoms in molecules (QTAIM) was fundamentally established as a valuable tool for the investigation of the nature of the interfacial interactions between organic molecules and metallic surfaces. The topological features of the electron density at the bond-critical point (BCP) provide quantitative information on the characteristics of a specific bond. In this work (P.M. Mitrasinovic, Technique-Tehnika vol. 60(4), pp. NM1-NM9, 2005), a general methodology for the determination of

the nature of the interfacial interactions is proposed by investigating the changes of the organic/metal bond-critical parameters as consequences of both increasing the size and changing the shape of the metal clusters. In particular, the adsorption of acrylonitrile (AN) on the copper (100) surface is analyzed by considering model clusters (Cu_n, n = 9-14,16,18,20) for the actual surface. Statistical models with their goodness of the fitting of the data obtained by use of the topological analysis of the charge density at the AN/Cu_n (n = 9-14,16,18,20) BCPs are reported. In getting these results essentially associated with the electronic properties and reactivity of various copper clusters, no reference to orbitals has been invoked.

COLL 259 Transfer of PTFE and PEEK-PTFE composites in tribological interfaces

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Understanding the mechanism of wear and friction for PTFE and PEEK-PTFE composites is necessary for establishing the conditions under which they can be used. To assess these mechanisms, surface analysis of PTFE, PEEK-PTFE composites and their transfer films were studied using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The chemical composition of the composite transfer film on stainless steel, as a function of wear cycle, has been determined through XPS and indicates that the amount of PEEK transferred to the surface is proportional to the number of wear cycles. Microscopic friction measurements of PTFE and the composites have been obtained using AFM and compared with macroscopic friction measurements using a reciprocating pin-on-disk tribometer. These results highlight the importance of fibrilation in transfer and friction processes.

COLL 260 Tunable charge transfer properties across thin-layers of Au nanoparticles

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Solution electrochemistry of small Au clusters is well characterized, revealing interesting quantized double-layer charging/discharging behavior; however, when the Au nanoparticles (NPs) are organized as multilayers on supporting electrodes, new fascinating phenomena appear. In our research, thiol-protected Au NPs are deposited as thin-layers on working electrodes using a drop-casting technique and the charge transfer properties of the resulting assemblies are studied by electrochemical methods. For 2 nm Au NPs, we observed that the electron transfer across the thin-layers can be controlled by manipulating the ligand chain length (C6, C8 or C12), the applied potential on the working electrode or the environment (aqueous/organic solvent, electrolyte, solution ionic strength). The implications of the potential and environment-dependent charging properties of the Au thin-layers will be discussed in the perspective of developing new nano-structure based devices.

COLL 261 Tunable porous gold surfaces created by self-assembly of gold nanoparticles with polyhedral oligomeric silsesquioxane (POSS) at different temperatures

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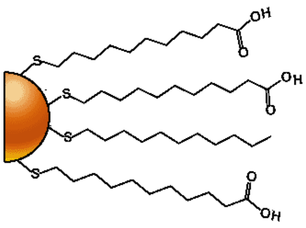
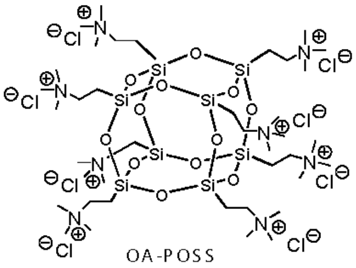
Hybrid inorganic/organic composite materials composed of gold nanoparticles (6.8 nm) and polyhedral oligomeric silsesquioxane (POSS) units were created using electrostatic self-assembly. The naocomposites were then used to create porous gold surfaces with different pore sizes based upon the temperature they were annealed. The silica of POSS surrounded by gold was etched out by 5% HF solutions. The porous gold surfaces were analyzed for surface morphologies by Atomic force

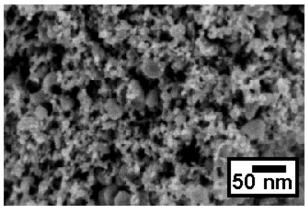
microscopy (AFM) and Scanning electron microscopy (SEM). The porosity of the gold surfaces created at various temperatures was also tested through cyclic voltammetry (CV) to study the difference in conductivity of gold and diffusion rates. These nanoporous gold surfaces can have tremendous amount of applications in the field of biofuels and biocatalysis.



Gold nanoparticle



Polyhedral oligomeric silsesquioxane (POSS)



SEM image

COLL 262 UV-vis and ^{19}F NMR determinations of critical micelle concentrations of ionic and non-ionic surfactants

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A convenient method for the determination of critical micelle concentration (CMC) of ionic and nonionic surfactants, in the presence of a room temperature ionic liquid (RTIL), has been developed using UV-vis spectroscopy and N,N-dimethyl-4-[(4-trifluoromethyl)phenylazo] aniline (1), a fluorinated dye. It is a relatively more sensitive and reliable method for the CMC determinations, requiring only small concentrations of the dye. The current methods extend our earlier UV-vis methods for CMC determination using 8-anilino-1-naphthalenesulfonic acid as the dye. The latter method is limited for the CMC determination of ionic surfactants. Further, using the compound 1, we were able to use ^{19}F NMR spectroscopy to determine the CMC values of SDS in the presence of an RTIL. The latter method serves as a complementary method to the one using UV-vis spectroscopy.

COLL 263 Wetting behavior of water droplets on microstructured surfaces

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Using lithographic techniques, we have fabricated a collection of silicon-based post surfaces where post size d and post spacing s have been systematically varied between 4 and 32μm. Besides the geometric parameters Φ (solid fraction) and r (roughness factor), a post surface is characterized by the equilibrium contact angle of the surface coating, Θ^e. We have additionally controlled Θ^e by coating the silicon surface with thin films of various polymers. In our contact angle experiments, we were particularly interested in observing the transitions between the different wetting states, i.e. the Cassie, Wenzel and superwetting regimes. When comparing the results to existing models, we found good agreement for the hydrophobic region. In contrast, for the hydrophilic region we report a number of unexpected effects, such as the existence of metastable Cassie drops which are stabilized by a kinetic barrier.

COLL 264 Writing with molecules at the nanoscale via automated scanning probe lithography: Design and construction of 2-D arrays of nanopatterns

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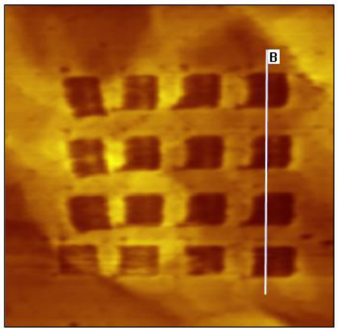
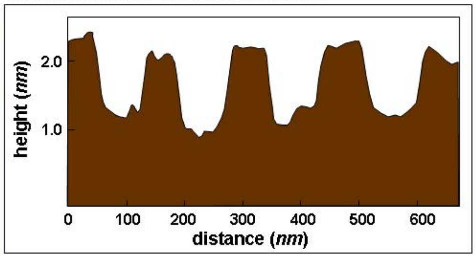
Modern commercial atomic force microscopes (AFM) typically include software with capabilities to control the length, direction, speed, bias pulse duration, residence time, and the applied force of the scanning motion of the AFM tip, analogous to a pen-plotter. This enables new capabilities for control and automation to manipulate molecules on surfaces via scanning probe lithography (SPL) – with angstrom precision. Nanopatterning with SPL is comparable to writing with a pen on paper; with the SPL tip as the pen, the self-assembled monolayer (SAM) as the ink, and the substrate as the paper. Self-assembled monolayers of n-alkanethiols are convenient molecules for “writing” chosen functionalities on gold surfaces. Automation provides high reproducibility, exquisite spatial control, and enables complex nanopattern arrays to be rapidly created. Usually, less than 1 minute is required to fabricate each nanopattern. Example AFM images will be presented of arrays of nanopatterns written using nanografting of SAMs with various chain lengths and terminal chemistries.





Array of 11-mercaptoundecanoic acid nanopatterns (100 x 100 nm^2) written in a matrix SAM of octadecanethiol.

COLL 265 A universal substrate for bio-functionalization

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Self-assembled monolayers (SAMs) possessing surface energy gradients have proven to be a versatile substrate useful for examining numerous physical and biological phenomena. Further extension of these methods includes the characterization of surfaces possessing well-defined gradients of bio-active peptides designed to control cell adhesion. Our approach to the fabrication of bioactive surface gradients has been to develop and characterize a “universal substrate” to which various species can be attached. The Huisgen [3 + 2] cycloaddition between terminal alkynes and azides to generate substituted 1,2,3-triazoles has seen widespread utility of late due to its high degree of dependability, complete chemical specificity, and the relative bio-compatibility of both the reactants and reaction byproducts. This approach may lead to methods for measuring cellular responses and improved tissue formation in tissue engineering applications. The syntheses, characterization and biological assessment of bioactive films possessing gradients in RGD peptides will be described.

COLL 266 Control and modeling of protein adsorption in microfluidic devices

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We are investigating the adsorption of proteins under static and dynamic fluid conditions in MEMS devices, and the different effect this has on protein/surface interactions. The long-term combination and integration of biological and electronic components requires a thorough understanding of surface/biomolecule interactions in these systems. The use of surface modification techniques allows us to tailor the interface between biological/nonbiological materials, independent of the bulk composition of the nonbiological material. We are developing modeling tools, in conjunction with our experimental results, for predicting the interactions of proteins with microsystems under static and flow conditions with the goal of creating biocompatible MEMS devices that can be easily integrated with these biologically based systems. Our results to date have indicated we can measure protein adsorption down to less that 1% of a monolayer and that static results are very different than those observed under flow conditions. Thus, data obtained under static conditions cannot be used as a predictor for behavior under flow conditions.

COLL 267 Fabrication of bioconjugated polymeric nanostructures and metal nanowires by electric field-induced scanning probe lithography

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Patterning of polymeric and biomolecular nanostructures on surfaces and the control of their architecture are critically important for the fabrication of biomolecular devices and sensors. Here we show how we use field-induced scanning probe lithography (FISPL) to chemically modify polymer brushes directly to allow conjugation of biomolecules. Surface-confined non-fouling and protein resistant poly(oligo(ethylene glycol) methyl methacrylate) (pOEGMA) brushes were prepared on silicon substrates by surface-initiated atom transfer radical polymerization (ATRP) in a *grafting-from* approach. These pOEGMA brushes were then patterned directly on the nanoscale by AFM anodization lithography, generating nano-trenches with carboxylic acid functionality. Proteins were then immobilized on these nanopatterned areas by suitable coupling chemistries. We also show an intriguing approach to deposit gold onto silicon oxide patterns by field-emission from gold-coated AFM probes. We capitalize on this novel lithography approach to fabricate gold nanowires of arbitrary shape. Our unique nanofabrication approaches lead to novel types of nanostructures that can potentially be used as biosensors or as substrates for the precise presentation of biomolecular queues to cells. Furthermore, our gold nanostructures can be used for electrical connections, or as plasmonic structures for biomolecular sensing.

COLL 268 Waveguides in metal nanoparticle arrays

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Taking the advantage of the coherent coupling among metal nanoparticles in one dimensional arrays, we propose a waveguide device which can turn light 90 degrees with high efficiency. Also, appropriately optimized array structures enable the propagation of plasmonic excitations for hundreds of microns. The influence of particles size, number, and surrounding environment on efficiency of this waveguide structure is also discussed.

COLL 269 Growing gold nanoparticles in dumbbell shape amphiphile dendrimer hydrogel

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Gold nanoparticles are prepared in a hydrogel template which is made of a dumbbell shape amphiphile dendrimer. The process is simple. No heating, agitation and stabilizers are necessary. Gold nanoparticles with size below 50 nm are formed under atmospheric conditions. The dendrimer acts as both reducing reagent and stabilizer. Along with the growing of gold nanoparticles, the gel is

weakened and the straight, unbranched, long and thin fibrils turned into irregular, smaller structures. The mechanism is discussed. As an application, the method is used to grow gold nanoparticles in a temperature sensitive hydrogel, PNIPAM gel. The gold ions are reduced by the dendrimers and there are no covalent bonds between gold and PNIPAM gel. The product had a phase transition temperature in the same range as that of the pure PNIPAM gel. The light transmittance of the PNIPAM gel was modified by the forming of gold nanoparticles.

COLL 270 Multi-functional core-shell nanoparticles self-assembled from amphiphilic copolymers for intracellular anticancer drug delivery to cancer cells

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We have recently developed pH-induced temperature-sensitive core-shell nanoparticles self-assembled from poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide-co-10-undecenoic acid). These nanoparticles are stable in the physiological environment but deform in acidic solutions (i.e. endosome and lysosome), releasing the enclosed drug molecules [1]. In this study, cholesterol is attached to the hydrophobic segment of the polymer, and folate, which can recognize cancer cells over-expressing folate receptor, is conjugated to the hydrophilic segment. This amphiphilic copolymer is self-assembled into core-shell nanoparticles having a stable core and a shell containing folate molecules. Doxorubicin, an anticancer drug, is readily encapsulated into the nanoparticles, and drug molecules are rapidly transported to the cell nucleus. The uptake of nanoparticles by folate receptor-positive cancer cells is much higher than that by folate receptor-deficient cells, resulting in greater cytotoxicity of doxorubicin against the former cells. Using these core-shell nanoparticles, anticancer drugs can be targeted to cancer cells and released intracellularly for efficient cancer therapy.

[1] K. S. Soppimath, C. W. Tan and Y. Y. Yang. Advanced Materials 17 (2005) 318-323

COLL 271 Polyelectrolyte multilayers with ultrahydrophobic properties

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A highly fluorinated polyelectrolyte, poly(4-vinyl-tridecafluorooctyl pyridinium iodide)-co-poly(4-vinyl pyridine), P4VTDFOP-co-P4VP was synthesized and used to assemble ultrathin films of polyelectrolyte - Nafion combinations that were hydrophobic with surface advancing contact angle of 114°. These films were characterized and compared to three different multilayer systems: Nafion-PDADMA, PSS-PFPVP, and PSS-PDADMA. Permeability measurements of P4VTDFOP-co-P4VP multilayer combinations were studied using a rotating disk electrode (RDE) voltammetry with both potassium ferricyanide and potassium iodide as probe ions and with varying the salt concentration. The membrane-limited current and the corresponding flux and diffusion coefficient of probe ions through thin films were calculated. Fourier Transform Infrared Spectroscopy-FTIR measurements were used to determine water content inside Nafion-PFPVP films, and the result was compared to the above three polyelectrolyte systems. Furthermore, the positively charged polyelectrolyte was used to assemble ultrathin films of polyelectrolyte - clay combinations that were ultrahydrophobic with surface advancing contact angle of 168°.

COLL 272 A perfectly hydrophobic surface

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There has been renewed interest in synthetic ultrahydrophobic surfaces and simultaneous control of surface chemistry and topography has recently been used to prepare an enormous number of examples of surfaces that shed water droplets easily. Many groups now use the criterion of a contact angle greater than 150° for labeling a surface “superhydrophobic.” This will be criticized in this talk. We have prepared a number of nearly perfectly hydrophobic surfaces with advancing and receding contact angles greater than 176°. We will report and show movies of one with advancing/receding = 180°/180° that can be prepared quite easily. Central to this work was developing a new method to measure contact angles, one that can distinguish a 178° advancing angle from a 180° advancing angle. This new technique will be reported as well.

COLL 273 Adsorption of polymers onto patterned surfaces: Novel opportunities provided by self-adoptive polymer brushes

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We theoretically investigated the adsorption of polymers onto mixed brushes that are formed by two incompatible polymer species covalently tethered to a solid substrate. Adopting to a given solvent quality, the outer adsorbing surface of the mixed brush assumes random, striped or homogeneous pattern. Our work aims at theoretical understanding of that how the formation of such patterns on the adsorbing surface of mixed brushes affects the adsorption of selected homo- and copolymers. By making use of the self-consistent field theory we calculate density profiles and adsorbances of adsorbed polymers for each of the above described surface patterns. Different affinities between adsorbed polymers and the polymeric species forming the mixed brush are considered, as extracted from the experimental data. The calculations are performed for homo-polymers, as well as random polymers that mimic selected bio-proteins. Our theoretical finding are compared against the performed Monte-Carlo simulations and available experimental results.

COLL 274 Biomolecular patterning using scanning near-field photolithography

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Directed immobilization of biomolecules on surfaces can be achieved by the patterning of organic thin films, to produce regions of contrasting biological adhesiveness. Monolayers of organothiolates on gold can be selectively oxidized by irradiation with UV light to yield weakly bound sulfonates, which are then displaced by solution-phase thiols with contrasting functionalities. The patterning of regions as small as 9nm has been realized using Scanning Near-field Photolithography (SNP), whereby a Near-field Scanning Optical Microscope (NSOM) is coupled to a UV laser to initiate photochemical reactions. Rates of photo-oxidation of organothiolate SAMs correlate to the surface potential of the SAM, which is dictated largely by the polarizability of the tail group. Biological adhesiveness is also dictated by the nature of the tail group. Plasma proteins are resisted by oligo(ethylene glycol) terminated SAMs, while bacterial light-harvesting antenna complexes, which reside in lipid membranes, have been better patterned by modifying the surface free energy.

COLL 275 Colloidal organic light emitting diodes

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In recent years the importance of the organic light emitting diode (OLED) has grown immensely. They have proved very desirable in numerous applications because of their very high efficiencies, low power consumption, and ease of fabrication. In view of these advantages it would be highly desirable to produce a white-light emitting OLED. Typically, these devices have been constructed in a layered, thin film fashion consisting of electron and hole transport materials doped with a luminescent dye. By changing the dye it is possible to tune the emission of the OLED to particular wavelengths. However to produce a white light emitting OLED, simple blending of the various dyes with the host material results in drastically reduced performance due to energy transfer between the various dye molecules. To achieve maximum efficiency the dye molecules should be separated by some distance. We propose here forming hole transport, electron transport materials and appropriate dye molecules into colloid particles. Using this method, it is possible to create individual colloid particles which emit in the red, green, and blue regions of the visible spectrum. If three appropriate colloid particles are mixed and deposited into a thin film, the resulting separation of the dyes would reduce undesirable energy transfer. This method should prove a viable pathway to a simply constructed white-light emitting device.

COLL 276 Colloidal polyelectrolyte complexes for targeted drug delivery to vascular endothelial cells

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Water-soluble, nanoparticulate, polyelectrolyte complexes (PECs) are desirable due to the biocompatibility and biodegradation of the constituent polymers. PEC properties depend on concentration, ionic strength, pH, and molecular parameters of the polyions. The complexation process between polyelectrolytes having significantly different molecular weights leads to the formation of water-insoluble aggregates. PECs were prepared and compared using systems with similar and dissimilar molecular weights, with the primary goal being a functionalized PEC system for effective targeting and uptake by vascular endothelial cells. PECs formulated from precursors with similar molecular weights yielded particles with suitable physicochemical characteristics and stability across a wide pH spectrum, as verified by both photon correlation spectroscopy and TEM. Biological activity, specifically binding and internalization kinetics for receptor-targeted and non-targeted PECs, was established by confocal microscopy, fluorescence associated cell sorting (FACS), and near-infrared imaging. These approaches will help define vascular cellular uptake mechanisms.

COLL 277 Comparison of polyelectrolyte multilayers built by spin coating and inverted spin coating

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The electrostatic self-assembly method for deposition of multilayer thin films could be drastically improved by a spin-coating technique with shorter preparation times and smaller volumes of building polyelectrolyte material needed. This presentation compares the traditional multilayer inverted spin coating by dipping with a novel method of poly(styrenesulfonate) and poly-(diallyldimethylammonium) solutions. A highly uniform thin film is rapidly obtained. We examine the influence of priming layers, different salt concentrations of the building polyelectrolyte solutions and different spinning velocities for the substrate. All these factors are investigated and compared to their effects on the conventional inverted spin coating by dipping technique. If in fact plain spin coating can achieve similar properties in robustness and evenness of built films it could have a major impact on multilayer thin film buildup or simple introduction of particles into the film and it would bring the polyelectrolyte multilayer field a step closer to industrial applications.

COLL 278 Controlled release biomaterial nanoscale coatings by stepwise deposition of silk fibroin

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There is a critical need in the field of biomedicine and tissue engineering to develop simple and versatile methods to assemble biocompatible and functional advanced biomaterial coatings. In this presentation, a completely aqueous, stepwise deposition process with Bombyx mori silk fibroin for the assembly of nanoscale drug controlled release thin film coatings will be discussed. Model compounds representing small molecular drugs, therapeutic relevant peptides, and proteins were used to study the incorporation and release behavior. The focus of this work was to develop an understanding of the control of the structure and morphology of the coatings and the release kinetics of the bioactive molecules from a physicochemical perspective. The silk fibroin adsorption process was stable and reproducible, with control of a single layer thickness ranging from a few to tens of nanometers, determined by the concentrations of silk fibroin, salt concentration in the dipping solution, and method of rinsing. The driving force for the assembly of silk fibroin onto the substrate was primarily hydrophobic interactions, while some electrostatic interactions were also involved. The structural control of the silk protein locks in the features of the coatings due to the physical cross-links (beta sheets), providing robust material features. This approach offers new options to engineer biomaterial coatings as well as bulk materials with control of both interfacial properties conducive to specific cellular or tissue responses and the potential to entrap and deliver labile molecules or other components due to the all-aqueous process described.

COLL 279 Core-satellite nanoassemblies with designed plasmonic properties

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The plasmonic properties of metal nanoparticle (MNP) assemblies composed of satellite particles tethered to a core particle have been investigated. Biomolecular tethers composed of thiol- and/or biotin functionalized DNA were used to link satellite particles to cores dispersed in solution or attached to a substrate. The dependence of the plasmon resonance of the coupled assemblies on hybridization state of the DNA was investigated using (1) single stranded DNA (a'b') that includes a sequence complementary to the tether strands as well as a toehold (a' and b', respectively) (a) to form duplex and (2) a single stranded competitor strand (ab) to dehybridize the tethers. Extinction and scattering spectra of the assemblies were compared to spectra calculated using structural models parametrized in terms of satellite coverage and spatial distribution.

COLL 280 Creating macroporous voids in silica aerogels

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Macroporous materials with very open networks improve separation efficiencies by preventing deleterious pore blocking thus enhancing mass transfer properties. Silica aerogels are open-celled foams exhibiting open pore networks with narrow pore size distribution (2-50 nm) and high surface areas (~ 900 m^2/g). Their small pore size and narrow pore size distribution, while important in certain applications such as insulators, absorbents, molecular separations, also restricts the use of aerogels in applications for catalysis for shape selection, diffusion of reagents, and biotechnology applications. The work presented details our efforts to create new hybrid hierarchical macroporous silica aerogels. These new macroporous aerogels were formed utilizing polystyrene beads (PS)

varying from 50 nm to 2 micrometer in diameter, dispersed into a TMOS or 1,6-bis(trimethoxysilyl)hexane sol-gel solution. Following gelation of the sol, the gel was super-critically dried in CO_2 creating a silica aerogel templated with PS beads. The PS beads were removed by solvent extraction or slow thermal treatment creating meso- to macroporous voids in the silica aerogel monolith.

COLL 281 Directly measuring the adhesive and elastic properties of bacteria using a Surface Force Apparatus: Effect of desiccation

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Bacteria can survive exposure to harsh conditions such as drying. Desiccation is one of the most severe stresses and can damage DNA. Therefore, bacteria have developed strategies to protect against dehydration. Evaporative deposition of bacteria on a surface shows that some bacteria aggregate to form two dimensional patterns which may be important for survival in dry conditions. For a decade, Atomic Force Microscopy (AFM) has been the primary tool used to study the adhesion and elasticity of individual bacteria. In this work we show it is possible to use a Surface Forces Apparatus (SFA) to measure the adhesion and elasticity of surface bound bacteria. The measurements are conducted with incomplete, patterned bacterial films and a protocol has been developed to image the contact area with AFM after the experiment. We measured the force profile between a Pseudomanas Aeruginosa PAO1 film and a bare mica surface with SFA.

COLL 282 Dynamic tuning of organic lasers with colloidal crystals

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The prospect of an inexpensive organic laser which can dynamically (i.e. in real time) alter its lasing wavelength is desirable for a number of display and communication technologies. Extensive efforts have focused on developing liquid crystal-based or polymer based lasers which can exhibit emission tuning through the application of an external stimuli, ranging from a mechanical stress, a temperature variation, or a radiation exposure. Although these system are promising, they often require an extensive synthetic effort to produce the gain medium or complicated interference lithography to form the grating. In this study we report on the utilization of colloidal crystals to provide the required reflectivity in an external resonator cavity laser design. By utilizing the mechanochromic effect, the crystalline colloidal array can be used to tune the lasing wavelength of an organic thin laser over 30 nm.

COLL 283 Effect of hydrophilic polymers on the competitive adsorption of model lung surfactant and serum proteins

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The effect of hydrophilic polymers on the competitive adsorption of model lung surfactant (LS) and serum proteins is investigated with a Langmuir trough, fluorescence microscopy and quantitative Brewster angle microscopy. These experiments are compared with a novel diffusion plus potential energy barrier theory for LS adsorption based on Smoluchowski's theory of slow colloidal aggregation. While the serum proteins increase the potential energy barrier due to steric and

electrostatic effects, the polymer generates a depletion potential to reduce the energy barrier. Results show that LS adsorption scales with polymer concentration and molecular weight as predicted. Fluorescence images show distinct changes in morphology as LS adsorption increases while Brewster angle microscopy gives insight into relative adsorption rates. This work has applications in developing a next-generation, inactivation-resistant LS which will serve as therapy for lung diseases such as Acute Respiratory Distress Syndrome.

COLL 284 Exchange dynamics in nanocapsules monitored by NMR diffusometry

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Nanosized core-shell particles having a liquid hydrophobic interior and a cross-linked polysiloxane/silica shell are able to sequester hydrophobic guest molecules. A potential application of the nanocapsules is for drug detoxification purposes. The size and the surface properties may be altered in order to optimize different detoxification purposes.

The NMR diffusometry method was utilized to investigate component resolved diffusion constants of differently prepared core-shell particles dispersed in water.

The results show that NMR diffusometry is a suitable method for studying particle size (obtained from diffusion rate) and dynamic phenomena, such as exchange rates of molecules that diffuses between the inside and the outside of core-shell particles having a porous shell. The results render the possibility of making a detailed description of the dynamic exchange of molecules such as toxins.

COLL 285 Fabrication and study of nanoparticles with hydrophobic/hydrophilic behavior

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Nanoparticles and colloids with grafted polymer brushes represent a numerous class of responsive materials relevant to the broad range of applications: stimuli mediated drug delivery, reversible encapsulation and/or release of medicines, diagnostics, sensors etc. Here we describe the fabrication and investigation of smart responsive nanoparticles by grafting block copolymers. We grafted either triblock copolymer of poly(styrene-b-2-vinyl pyridine-b-etyleneoxyde) or diblock copolymer poly(styrene-b-4-vinyl pyridine) to silica particles with diameter of 200nm. We obtained smart coatings with responsive switching behavior upon exposure to different solvent. The texture of the deposited coatings can be regulated via tuning the particle aggregation in the aqueous solutions with added selective solvent for PS (toluene). We used pH as an adjusting parameter to tune sizes of particle aggregates. An increase of pH values allowed us to fabricate larger aggregates of the particles. The switching of surface properties was investigated by AFM and water contact angle measurements.

COLL 286 Flow–through electrogenerated chemiluminescence in polyelectrolyte multilayers

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Electrogenerated chemiluminescence is an electrochemically induced process in which light is emitted from an excited species. Excitation is achieved by direct oxidation of luminescent species (tris(2,2')bipyridylruthenium), or indirectly, by using an intermediate or coreactant (tripropylamine). The use of polyelectrolyte multilayer film coatings with electroluminescent systems becomes an intriguing choice for electrode modification and superior luminescence efficiency. Polyelectrolyte multilayers were also investigated by observing the luminescence with varying NaCl and tripropylamine concentrations in the electrochemical cell solution. In the present case, Ru2+ is converted to Ru3+ at the electrode surface. Since the electrochemical current at 1.19 V has not yet reached the diffusion limited case (where the surface concentration of Ru2+ is 0), the oxidation rate of Ru2+ is mainly limited by charge transfer kinetics. The Ru3+ that is produced, however, is limited much more by diffusion and therefore accumulates within the film, where it reacts with tripropylamine.

COLL 287 Highly specific capture of proteins on aptamer monolayers

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Aptamers are oligonucleotides selected from combinatorial libraries by an in-vitro iterative process. Aptamers bind to various target compounds with high affinity and selectivity. Use of aptamers for protein recognition instead of antibodies is of particular interest, because the specificity and affinity of aptamers are comparable to that of antibodies. Furthermore, aptamers demonstrate greater stability on surfaces, making them particularly suitable for biosensing applications. We prepared mixed self-assembled monolayers (SAMs) on gold surfaces incorporating an aptamer elicited toward thrombin as a model system to develop immobilization strategies for maximizing aptamer affinity and selectivity. In this work the effect of the length and the nature of the linker connecting the aptamer sequence to the thiol moiety, and the nature of the co-adsorbent on the specificity and affinity on thrombin binding, will be presented.

COLL 288 Hydrogel encapsulated membranes

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Planar lipid bilayer membranes are commonly used to contain membrane channel proteins for biophysical studies and sensor applications. Significant drawbacks to their use include limited lifetime and mechanical instability. Tethering membranes to solid supports has been shown to increase membrane lifetime; however it is difficult to obtain single channel data with supported membranes. Although some promising work has been done with membranes spread onto pre-cast hydrogels, hydrogel-based membrane supports have not been capable of combining long membrane lifetimes with single channel data. We have encapsulated lipid bilayer membranes in a hydrogel via in situ polymerizaion. These encapsulated membranes show improved mechanical stability and have sustained continuous measurements of single channels over 5 days, demonstrating their potential to extend the scope of channel protein experimentation and to enable sensor applications. Preliminary work has also shown slowed translocation of single stranded DNA through incorporated channels, possibly enabling electrical detection of single bases.

COLL 289 Interrogations of microgel multilayers by optical and acoustic measurements

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A series of studies on thin microgel films using both quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) are described. Thin films composed of pNIPAm-co-AAc microgel core particles or pNIPAm/pNIPAm-co-AAc core/shell particles were constructed using spin-coating layer-by-layer (scLbL) assembly with poly(allylamine hydrochloride) (PAH) as a polycationic “glue”. Behavior of the films has been characterized for low film thicknesses (~1 ìm or less). The findings suggest that the interaction between the negatively-charged particles and the positively-charged PAH has a significant effect on the pH responsivity and the optical and mechanical behavior of these films. The most significant changes in behavior are observed in the resistance data from the QCM experiments. Slight changes the film composition and alternating the pH of the environment around the film changes the responses measured by the QCM more significantly then expected. The SPR data support these observations. Together, these studies allow for a deeper understanding of the morphological changes that take place in microgel-based thin films; such changes may be of utility in the design of highly sensitive transducers of biomolecular binding events.

COLL 290 Microemulsion based hydrophobic-core hydrophilic-shell nanoparticles: Physical characterization and study of their potential use as encapsulating agents

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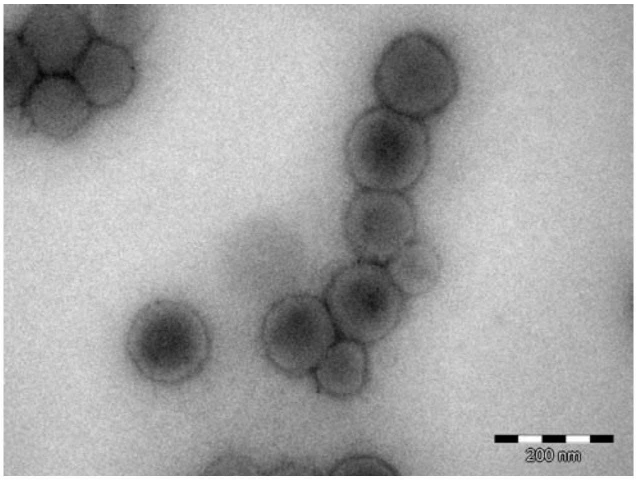
A ternary surfactant system was used for the synthesis of hydrophobic-core hydrophilic-shell nanoparticles. A chemically active surfactant functioned as anchoring points for the growth of the shell on the surface of the particles. Different techniques were used to characterize their size and the physical properties of the core and the shell. It was observed that when deposited on a substrate, the particles expand to a different degree depending on the polarity of the substrate. Two hydrophobic dyes, dansyl chloride and coumarin 153, were used to prove the ability of the particles to encapsulate hydrophobic compounds. The dye emission was analyzed, showing that after encapsulation the dye molecules reside in a non polar microenvironment, isolated from the polar solvent. Uptake of these fluorophores by the core-shell particles from aqueous suspensions was successfully performed, showing that they could be used for removal of different agents of low polarity from aqueous systems



COLL 291 Minimizing the density of polymer crosslinked aerogels

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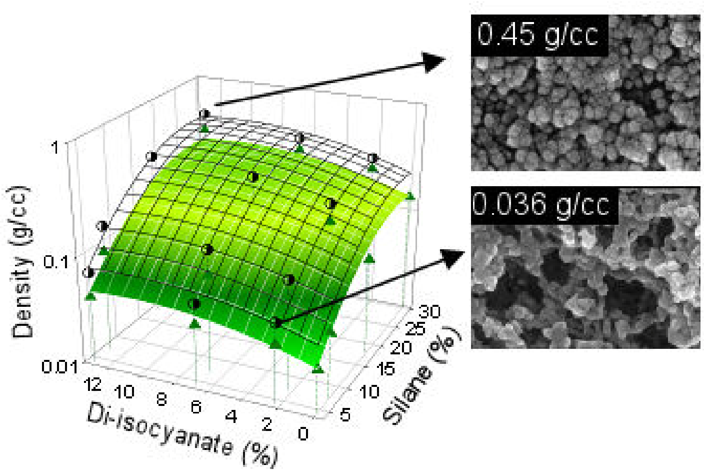
Polymerization of a di-isocyanate with the surface amino groups of a sol-gel derived mesoporous silica network crosslinks the nanoparticles of the silica skeleton, and reinforces the otherwise fragile underlying framework. Systematically adjusting the processing variables effecting density produces aerogels whose macroscopic properties such as stress at failure and modulus could be controlled, and are attributed to changing morphology on the nanometer scale (see figure below). The lowest density crosslinked aerogels (~ 0.036 g/cm^3) exhibit a forty-fold increase in strength over the corresponding non-crosslinked framework, and are flexible. Flexibility is a property that aerogels have not previously exhibited, and thus indicates that at very low silica content, the properties of the polymer crosslink begin to dominate those of the rigid silica framework.



COLL 292 Nanoparticles from chitin: Isolation, topochemical modification and its characterization

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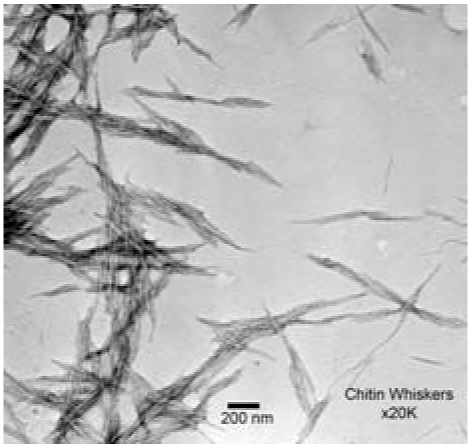
Chitin, a linear polymer of (1-4) linked ß-D N-acetylglucosamine, is widely found in a arthropod exoskeletons and fungal/ microbial species. In vivo, chitin exists in a nanofibrillar form in protein polysaccharide nanocomposites. In this report we discuss the release of chitin from its native structures, surface modification with short chains of poly-caprolactone (PCL) and characterization of both the native and modified materials by x-ray diffraction (crystallite size, degree of crystallinity and crystal allomorphic form) , transmission electron microscopy (particle size) , solid state CP/MAS and HR/MAS NMR (modification of surface chemistry and interactions between the PCL sidechains and the chitin backbone, thermal analysis and surface area measurements. Fig. 1 shows partially dispersed chitin particles prepared from shrimp exoskeletons. Preliminary results for the interactions of these particles with a poly hydroxyl alkanoates matrix also may be discussed.



COLL 293 Nanostructured polymer conetworks and nanotemplating thereby

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A series of new polymer conetworks consisting of covalently bonded immiscible polymer chains, especially hydrophilic and hydrophobic polymers to form amphiphilic conetworks, has been synthesized by applying telechelic macromonomers and special synthetic strategies. Systematic structural studies have revealed unique cocontinuous (bicontinuous) nanophase separated morphologies. Utilizing such nanostructures as templates, various new hybrids composed of nanocrystals of inorganic materials embedded in the conetwork nanophases have been prepared and investigated.

COLL 294 Observability of local dielectric variation as detected by nanoparticles of various shape

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Electrodynamic calculations of nanoparticle spectra are used to investigate the refractive index sensitivities and widths of surface plasmon peaks of gold nanodisks, nanorods and hollow nanoshells. Previously, the refractive index sensitivities of plasmon band position were found to increase linearly with band position, when band position is expressed in terms of wavelength. Here, we present quality factor modulated sensitivities. Quality factor, the ratio of band position to band width, is important when considering peak location sensitivity, as a large shift of a wide plasmon band may be undetectable, while a small shift of a narrow plasmon band is easily detectable. Because the radiative processes that broaden nanoparticle plasmon bands increase with particle volume, quality factor modulation lowers the refractive index sensitivities of particles elongated in one or more large dimension. Shape-dependent maxima in quality factor modulated refractive index sensitivities are identified for 12 nm thick disks, 20 nm diameter rods, and nanoshells of various thicknesses.

COLL 295 Organosilicate nanostructures from diblock copolymer micelles

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Self-assembly of block copolymers is a versatile phenomenon in the bottom-up approach for patterning surfaces and creating porosity at the nanoscale. Here we have used micelles and the inversed micelles from diblock copolymers consisting of polydimethylacrylamide and polylactide (PDMA-b-PLA) as templates for the fabrication of silica nanostructures. This was achieved by crosslinking of an inorganic precursor that is selectively miscible with the PDMA-block, being either on the inside or on the outside of the micelle depending on the solvent. Results on both thin and thick films from both types of micelles will be discussed, as measured by AFM, SEM, TEM, NMR, DLS and XRR.

COLL 296 Osmotic pressure effect on polyelectrolyte multilayers

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Poly(ethylene glycol) [(PEG(8000)], a neutral but highly water-soluble polymer, was used as an osmotic stressing agent to provide information about the water content of a polyelectrolyte multilayer (PEMU) made from poly(diallyldimethylammonium) (PDADMA), a positively charged polymer, and poly(4-styrenesulfonate) (PSS), a negatively charged polymer, on a germanium crystal. Attenuated total reflectance (ATR)-FTIR, performed in-situ on films that were thicker than the penetration depth of the IR light, was able to measure the change in the water content of a polyelectrolyte film exposed to aqueous solutions, and thus was used to provide information about water movement in and out of the film. The results obtained from (PEG) for this osmotic pressure experiment were compared to results obtained from using NaCl on the same film, considering the osmotic pressure of the salt solution.

COLL 297 Patterning of 100 nm wide lines of polymer brushes by controlled etching of polydimethylsiloxane

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We developed a method to pattern 100 nm wide lines of poly(5-norbornene-2-carboxylic acid) from monolayers on Si(111) by soft lithography. Olefin-terminated monolayers were assembled on Si(111) from a solution of $CH_2=CH(CH_2)_9O(CH_2)_9CH=CH_2$, 1-octadecene, and 0.1 mole % 2,2,6,6-tetramethyl-1-piperidinyloxy. These monolayers were reacted with the Grubbs' first generation catalyst to yield a monolayer terminated with this catalyst. A PDMS stamp with patterned microfluidic channels was placed on the surface and an olefin was passed through the channels. Next, the sides of the PDMS channels were etched with H_4NF to yield fresh, thin exposed monolayers terminated with the Grubbs' catalyst. Finally, a solution of 5-norbornene-2-carboxylic acid was added to the channels to grow patterned polymer brushes. Polymer brushes with widths of several micrometers to 100 nm were grown on these surfaces. This method is not limited by the wavelength of light and will, we believe, be extended to pattern smaller features on PDMS.

COLL 298 Plasma-enhanced synthesis of surfaces that kill bacteria on contact

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Covalent immobilization of polycationic structures onto organic and inorganic material surfaces is a key to develop stable antimicrobial surfaces. The surface layers that kill bacteria on contact are generated using low pressure, non-equilibrium plasma (LP-NEP)-enhanced synthesis and deposition of bactericidal quaternary ammonium thin layer macromolecular structures onto stainless steel and cellulose-based substrates. The stainless steel substrates are pretreated with O_2 and hexamethyldisiloxane plasmas to form an intermediate layer that stabilizes the bioactive top structure. The substrates are decorated with high densities of reactive nitrogen functionalities using ethylene diamine, acrylonitrile, or acetonitrile plasma. These films are covalently attached and do not delaminate by washing substrates with water or acetone. A subsequent *ex situ* reaction of the films with various alkyl halides generate quaternary ammonium groups and were confirmed by ESCA, FTIR, and GC-MS studies. The bactericidal properties of the surface layers are evaluated using standard colony counting procedures.

COLL 299 Polyelectrolyte multilayer swelling by different ions

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Polyelectrolyte multilayer (PEMU) layer by layer build-up of poly(diallyldimethylammonium) (PDADMA), poly(4-vinylpyridinium) (P4VMP), two positively charged polymers, and poly(4-styrenesulfonate) (PSS), a negatively charged polymer, was done on a germanium crystal, and attenuated total reflectance ATR-FTIR spectroscopy was used to provide information about the effect of the salt type on the thickness, water content, stability and behavior of multilayers. Fourteen different salts (including 4 IR active salts) were applied to PDADMA/PSS and P4VMP/PSS multilayers. Swelling due to water was measured, along with the number of intrinsic sites inside the 2 different multilayers. The number of residual extrinsic sites within the ultrathin films was determined from the ratios of IR active counter ions peaks and polyelectrolyte layer peaks. Quantitative estimates was made for the swelling constant ($K^{H_2O}_{salt}$), doping constant (K_{dop}) and the hydration numbers (H_2O_{hydrat}) for all ion pairs used. Also, poly(ethylene glycol) (PEG), a high osmotic stress agent, was used to provide information about water content of the PEMU.

COLL 300 Formation of oil filled silica shell nanocapsules and hollow silica nanoparticles using double microemulsion technology

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A novel and complementary method for the synthesis of oil core silica shell nanocapsules using an oil-in-water-in-oil double microemulsion is described. The characterization in terms of oil core and overall size was done by Quasi Elastic Light Scattering (QELS) and Transmission Electron Microscopy (TEM). The influence of surfactant nature and size on feasibility of the method is outlined. The importance of formulation parameters, surfactant-to-water and cosurfactant-to-water ratios on the overall size of nanocapsules is emphasized. The organic content of the nanocapsules is determined by Thermogravimetric Analysis (TGA). The calcination of organic content led to formation of the moderately polydispersed hollow silica nanocapsules that can be used in catalysis.

COLL 301 Protein-silica nanocomposites for drug detoxification purposes

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The synthesis of protein-silica nanoparticles (psn) using water-in-oil (W/O) microemulsion method is described. Characterization in terms of size, polydispersity and protein content was done by Transmission Electron Microscopy (TEM), Quasi Elastic Light Scattering (QELS), Infrared Spectroscopy (IR) and Thermogravimetric Analysis (TGA). The protein structure in the psn is compared to a native structure using NMR and IR. The drug binding properties of psn is demonstrated in vitro using HPLC in solutions of different pH and salinity. The partitioning of the drug was evaluated in human plasma and compared to pure silica nanoparticles, core-shell nanocapsules and pure protein solutions.

COLL 302 Reflex-arc on a chip: An in silico cell culture analog

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To overcome the shortcomings of in vitro and animal models we are developing a microscopic cell culture analogue (microCCA) of the spinal reflex-arc. The present work draws on advances in a wide variety of technical fields including cell culture, surface chemistry, and microfabrication. These advances have allowed us to begin development of a microCCA device comprised of the basic components of the reflex-arc: a muscle fiber, a dorsal root ganglion cell, and a motoneuron. Silicon microstructures serve as the foundation of the device. Surface modification with alkyl-silane SAMs followed by patterning with deep UV photolithography to selectively control cell adhesion and growth. Furthermore, we have demonstrated the control of neuronal growth and myotube differentiation on the microstructures. This system will enable the controlled interrogation of properties of the reflex-arc, thereby creating an improved test bed for the development of novel drug therapies for traumatic SCI and neurodegenerative diseases.

COLL 303 Single Channel activity from Gramicidin A ion channels in engineered tethered bilayer membrane arrays

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Sensors find use in a wide and rapidly expanding variety of applications. Recent chemical and biological threats, environmental concerns, and nanotechnology needs have only increased the interest in sensors capable of detecting analytes, such as toxins and drugs, over a wide dynamic range with high sensitivity and speed. Engineered membrane bound ion channels are promising biological receptors since they would allow for the stochastic detection of analytes at high sensitivity. For stochastic sensing it is necessary to be able to measure the ion currents associated with single ion channel opening and closing events. By interfacing the synthetic ion channel gramicidin A to a microelectrode array device we have been able to record single channel activity from gramicidin A in a tethered bilayer system. The stochastic response from trials where one, and two active channels were incorporated in the bilayer are compared.

COLL 304 Solution synthesis of PAMAM-stabilized platinum: Evidence for Pt-crosslinked dendrimers instead of zero-valent nanoparticles

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Many groups have used poly(amidoamine) (or PAMAM) dendrimers to synthesize solutions of noble metal nanoparticles based on what might be called the “templating hypothesis”. If true, this route offers unprecedented control over the nanopartiles' size, shape, and composition. Our work investigates the veracity of the templating hypothesis. We have studied the complexation of Pt precursor (K2PtCl4) with hydroxyl-terminated PAMAM (G4OH) using a variety of spectroscopic methods. The results show that although complexation of (PtCl4)-2 does not proceed to completion, the non-complexed Pt can be removed through dialysis. The presence of non-complexed Pt is critical to what happens in the subsequent reduction step using either NaBH4 or H2 gas. Reduction with NaBH4 has little effect on the Pt-PAMAM complex. For reduction with H2 gas, colloidal Pt particles appear if the non-complexed Pt is not removed by dialysis. If the non-complexed Pt is removed, reduction with H2 gas initially produces Pt dimers that remain coordinated with the PAMAM. Results from a variety of techniques, particularly liquid-phase EXAFS and XANES, suggest that the product is Pt-crosslinked PAMAM, not PAMAM-encapsulated, zero-valent Pt nanoparticles. Prolonged reduction with H2 gas eventually leads to arrested precipitation of colloidal Pt nanoparticles, but onset is delayed considerably due to the removal (by pre-dialysis) of the non-complexed Pt.

COLL 305 Sprayed polyelectrolyte multilayers

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Polyelectrolyte multilayers deposited by sequential or simultaneous spraying of poly(styrenesulfonate) and poly(diallyldimethylammonium) solutions are described. A highly uniform thin film is rapidly obtained over a large area. The morphology, uniformity, and chemical composition of sprayed multilayers as well as the selective membrane properties are found to be virtually identical to those prepared by dip-immersion. Films built without a rinsing step are thicker and subsequent layers do not adhere as strongly to each other. The force with which the polymer solution hits the target, along with the amount of time the film is allowed to rest on the substrate before a subsequent layer is added, are factors that influence the properties and formation of the thin film. A simultaneously sprayed film gains thickness in direct proportion with the amount of spraying time. The quality of the film depends on stoichiometric amounts of oppositely charged polymers being sprayed on the target area.

COLL 306 Surface modification of titanium with bioresistant polymer brushes

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Polymer brushes can be used to tailor the properties of surfaces that are important for the development of numerous biomedical applications. Here we describe an approach to modify the surface of titanium with self-assembled monolayers (SAMs) to fabricate multifunctional polymer brushes. Two-component SAMs of alkylsilanes bearing 2-bromopropionate and CH3 termini were prepared to conduct surface-initiated atom transfer radical polymerization (SI-ATRP) of oligo(ethylene glycol) methacrylate (OEGMA). SI-ATRP of OEGMA affords a dense layer of polymer that resists cell attachment. Modification of the hydroxyl end groups of the PEG segments of the brushes with bioactive peptide sequences such as fibronectin and collagen domains will allow for the investigation of different surface chemistries for biomaterials, regenerative medicine, and tissue engineering applications.

COLL 307 The sonication-aided encapsulation of Congo Red into a cationic micellar medium

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Congo Red is an organic dye that has been used not only as an acid-base indicator but also as a staining agent in biological systems. Although this dye is liberally soluble in water its fluorescence intensity is remarkable enhanced when solubilized in a micellar medium. We have used fluorescence technique to evaluate and characterize its encapsulation in a micelle of cetyltrimethylammonium bromide (CTAB) surfactant. It was observed that as much as 55 % of this dye molecule is encapsulated into the micelle with the aid of sonication. The observed fluorescence intensity was blue shifted from 413 nm in pure water to 405 nm in micelle. The spectral bandwidth measured at the FWHM is larger in aqueous phase than in the micelle by as much as 335 nm. The energetics of the transfer of this dye molecule from the water phase to the micellar pseudophase will be discussed together with the significance of this observation

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COLL 308 Well-defined pores in lipid membranes controlled by amphiphilic polymers

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Amphiphilic macromolecules can adsorb tightly on model biomembranes (e.g. lipid bilayers and giant vesicles) and locally perturb the lipid organization. An isolated macromolecule may permeabilize the membrane within a domain commensurate with the polymer radius, i.e. of nanometric size. Applications of such controlled pore-opening include drug release and mild permeabilization of living cells. We used phospholipid bilayers and short hydrophobically-modified polyacrylates (HMPs) to investigate non-deleterious permeabilization of biomembranes. We show that polydisperse and random synthetic copolymers can nevertheless form well-defined channels in membranes. The observation of giant vesicles by optical microscopy provided evidence for HMP-triggered leakage of macromolecular probes without membrane breakage. HMPs chemical structure, pH and ionic strength strongly influenced these properties. Electric conductivity measurements performed on black lipid membranes showed that HMPs stabilize pores with diameter of a few nanometres. As an application, efficient permeabilization of the periplasmic membrane of living cells will be briefly presented.

COLL 309 Infrared diffracting colloidal crystal tags using hard core/soft shell nanoparticles

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Microparticle spheres of poly-N-isopropylacrylamide (pNIPAm) can be utilized in the self-assembly of colloidal crystals that exhibit Bragg diffraction, which can in turn be used to develop coded optical tags. Because homopolymer pNIPAm particles are water-swollen, the resulting crystals lose their optical properties when dried. In order to produce robust optical materials, an alternative construct must be employed to provide structural stability. Copolymer spheres of polystyrene (PS)-co-pNIPAm have been synthesized to give more dense starting materials that yield a crystal with retained diffractive properties with subsequent drying. Using an additional synthesis scheme, a pure pNIPAm shell has been added to these hard cores that provides self-assembly via thermal annealing. Optical diffraction can be tuned based on particle size, and overall particle concentration. Simple drying techniques have also been employed to affect order between the particles. This hard core/soft shell architecture serves as a model for the generation of innovative optical materials.

COLL 310 Probing colloidal crystals with silver tracer nanoparticles

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The structure of colloidal crystals composed of thermoresponsive poly-N-isopropylacrylamide (pNIPAm) hydrogel nanoparticles has been investigated using silver tracer nanoparticles. Formation of a self-assembled crystalline network is achieved by heating a concentrated solution of pNIPAm particles above the particle's volume phase transition temperature of ~31°C to elicit a decrease in particle size, followed by reswelling of the particles using gradual cooling. A binary mixture can be achieved by adding small tracer nanoparticles of silver (~60 nm diameter) as a dopant prior to thermal annealing. This colloidal crystal gives rise to an arrangement in which the silver particles are positioned in the interstitial spaces between the pNIPAm particles. Caging of silver nanoparticles has been investigated using reflectance microscopy and particle tracking software to elucidate the structure and examine defects in pNIPAm colloidal crystals.

COLL 311 Multi-layered polyelectrolyte-microparticle coating for micro- to nano-scale capsules using optical trapping technique

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Since first introduced, encapsulation technology has experienced considerable progress both theoretically and experimentally. Core-shell microparticles have been applied extensively as microcapsules. Owing to their capability of encasing various materials, these capsules can be used for drug deliveries and sensitive agent protections. We have employed microfluidic devices and the laminar flow property involved to flow microparticles (as core) solution and the polyelectrolyte solutions (as shell) simultaneously. By the use of HOT (Holographic Optical Trapping) technique, large quantities of multi-layered polyelectrolyte coated microparticles can be formed inside the microfluidic devices and are ready for capsulation purpose. To monitor the growth of the layers and the film thickness, dynamic light scattering, ellipsometry and UV-Vis spectroscopy are used.

COLL 312 Direct nucleation studies of colloidal systems inside microfluidic droplets

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Even though the nucleation of crystalline materials is extensively studied, many aspects such as the dynamics of nucleation remain under hot debate, partly due to the limitations of experimental evidence. In this paper, emulsion droplets containing gel particles of a thermo-responsive polymer, poly-N-isopropylacrylamide(PNIPAM), has been used as an experimental model system for the study of nucleation. The polymer suspension is injected into a microfluidic channel together with two immiscible oil streams inside the outer channels to fabricate PNIPAM suspension droplets in oil. The concentration of PNIPAM gel particles is varied by temperature to determine the thermodynamic phase and the droplet size is varied using different flow rates of oil and colloidal suspensions to tune the nucleation volume. Here we present quantitative measurements of the nucleation process of colloidal systems using UV-Vis spectroscopy, light scattering and confocal microscopy. Effects of particle size and surface charge on the nucleation are also investigated.

COLL 313 Controlling PS-b-PEO morphologies by solution conditions

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We have investigated the self-assembly behavior of amphiphilic diblock copolymer polystyrene-b-poly(ethylene oxide) (PS-b-PEO) in DMF/water and DMF/acetonitirile mixtures. The morphology of the block copolymer can be controlled in both these systems by varying copolymer concentration and solvent composition. The morphologies were visualized directly by transmission electron microscopy. Increasing the water content in the DMF/water mixture or acetonitrile in the DMF/acetonitrile mixture changes the morphology from spheres to worm-like/rods and then to vesicles. Increasing the copolymer concentration shows a similar effect on the morphology. The block copolymer exhibits distinct phases of both exclusive and mixed morphologies. The morphological transitions were also captured by static light scattering and turbidity measurements. Although the trend in morphological changes is similar, there are remarkable differences in the morphological phase behavior of PS-b-PEO in these two solvent systems and thus the role of the ‘selective solvent' in such systems is also evidenced.

COLL 314 Influences of the ions of sulfonated lignins on gelation of poly(acrylamide-co-lignin) hydrogel

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In this presentation, we will showed recently prepared poly(acrylamide-co-lignin) hydrogels with different ions, e.g. Mg2+, Ca2+ and Na+. Discussions would be on the selection of the ions and these ions how to influence the sol-gel transition and gelation process.

COLL 315 Design of biodegradable amphiphilic polyphosphates with well-defined hydrophilic graft chains

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Polyphosphates as backbones were synthesized by ring-opening polymerization of 2-isopropyl-2-oxo-1,3,2-dioxaphospholane (IPP), 2-(2-oxo-1,3,2-dioxaphosphoroyloxyethyl-2-bromoisobutylate) (OPBB) and 2-choresteryl-2-oxo-1,3,2-dioxaphospbolane (ChOP) using triisobutylaluminium as an initiator. Three types of polyphosphates (PIBrxChy, x: number of OPBB units in a polymer; y: number of ChOP units in a polymer) such as, PIBr4, PIBr6Ch1, and PIBr3Ch2 were obtained. 2-Methacryloyloxyethyl phosphorylcholine (MPC) was grafted from the OPBB sites in PIBrxChy via atom transfer radical polymerization. On every polymer system, molecular weight of graft polymer is linear with conversion. The transition point (cmc) of the surface tension of the PIBrxChy-g-PMPCs aqueous solution decreased with an increase in the number of ChOP unit in a graft polymer. Particularly, PIBr3Ch2-g-PMPC14.7K formed nanosize-associates (Rh = 7.5 nm) with 2.2 molecules above 0.1 wt%. The cytotoxicity of graft polymers was evaluated using v79 cells and it was not observed. The graft polymers having cholesteryl groups effectively enhanced solubility of paclitaxel in an aqueous solution.

COLL 316 Effect of the ionic strength on the rheological properties of multisticker associating polyelectrolytes

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The rheology of hydrophobically modified polyelectrolytes containing small hydrophobic blocks randomly distributed along the hydrophilic backbone has been investigated in aqueous solutions by means of steady flow, creep and oscillatory experiments. The polymers contain acrylamide (≅ 86 mol %), sodium 2-acrylamido-2-methyl-1-propanesulfonate (≅ 12 mol %) and N,N-dihexylacrylamide units (≅ 2 mol %). The rheological behavior in the presence of electrolyte for two polymers with two different hydrophobic block lengths (N_H = 3 or 7 monomer units per block) was compared to that obtained for salt-free systems. At a fixed salt concentration, the critical concentration at the onset of the viscosity enhancement does not depend on the length of the hydrophobic segments in the polymers and is located in the vicinity of the critical overlap concentration of the corresponding hydrophobe-free polymer. This is in strong contrast to the behavior observed for the same polymers in pure water, for which the onset of the viscosity enhancement shifts towards lower concentrations as the hydrophobic block length is increased. Below the critical entanglement concentration (C_e) the presence of salt influences the dynamics of the polymers, resulting in a significant reduction of the zero-shear viscosity and of the plateau modulus, the terminal relaxation time being less affected by the addition of electrolyte. Near the C_e the presence of salt results in a strong shear thickening behavior, that is virtually absent in electrolyte-free solution. In contrast, in the entangled regime, the rheological behavior in salt solutions is not very different from that of the salt-free systems. The

properties of these associative polyelectrolytes have been analyzed in the framework of the available theories, that is, either the sticky Rouse model or the sticky reptation model, depending on the concentration range.

COLL 317 Interpolyelectrolyte complexes based on micelles of ionic amphiphilic diblock copolymers

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The interaction of micelles generated in aqueous solutions of ionic amphiphilic diblock copolymers, polyisobutylene-block-poly(methacrylic acid), with cationic polyelectrolytes results in the formation of novel water-soluble interpolyelectrolyte complexes. They represent peculiar polymeric architectures of core-shell-corona (″onion-like″) structure with a compact shell assembled from the coupled oppositely charged polyelectrolyte fragments. The original copolymer micelles appear to play a lyophilizing part in the complex particles, nearly not changing upon the interaction with cationic macromolecules. The responses of such complexes to the variations in pH and ionic strength of the surrounding medium were examined by means of variuos techniques, including turbidimetry, analytical ultracentrifugation, light scattering, small-angle neutron scattering, and time-resolved small-angle X-ray scattering.

COLL 318 Layer-by-layer self-assembled films of poly(3,4-ethylenedioxythiophene) nanoparticles and their biosensor applications

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A self-assembed multilayer film of poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles and a polyanion was prepared using the layer-by-layer (LbL) deposition method. The PEDOT nanoparticle has a cationic surfactant shell that gives positively charged surface. The electrochemical behavior and catalytic ability of PEDOT nanoparticle multilayer for the oxidation of β-nicotinamide adenine dinucleotide (NADH) were investigated by electrochemisty combinded with surface plasmon spectroscopy (SPS). The SPS curves changed when the polymer film was switched to different electrochromic states resulting from the change of dielectric constant and thickness of the PEDOT upon doping and dedoping. Furthermore, the films showed fast “ON/OFF” response upon switching between oxidation and reduction states. The PEDOT multilayer was successfully catalyzed oxidation of NADH, which was detected by SPS curve shift. The $\text{PEDOT}^{red}/\text{PEDOT}^{ox}$ steady-state ratio in the film was controlled by the concentration of NADH. Also, a LbL film of PEDOT nanoparticles and glucose oxidase was prepared and tested as a potential glucose biosensor.

COLL 319 Light-responsive emulsions triggered by complex mixtures of surfactants and azobenzene-modified polymers

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We describe an original emulsion system in which light rapidly transforms an O/W emulsion into a W/O emulsion by a simple switch between UV and visible irradiation. These properties are due to complex emulsifiers that combine the high sensitivity of photoresponsive macromolecules and the

ability of molecular surfactants to reversibly modify interfaces. Photochrome (azobenzene) side-groups confer to water-soluble macromolecules (polyacrylic acid based) an hydrophobicity which depends on their photo-isomerisation state. The macromolecules remain however essentially hydrophilic and could stabilise O/W emulsions. The surfactant properties enable stabilisation of W/O emulsion and light-responsive interaction with the polymers. We achieved light-triggered cycles of the direct-unstable-inverse sequence of emulsions under shear. At rest, the stability of emulsions was reversibly controlled by light. We demonstrate that limited change in hydrophobicity of polymers can be significantly amplified to be exploited in dispersions. Photo-triggering opens novel opportunities to control and study two fundamental properties of emulsions.

COLL 320 New chitosan hydrogels: Gelation mechanism and biological properties

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The gelation mechanism and biological properties of new hydrogel will be described. Theses materials are regarded as 'decoys' of biological media, as a result of their chemical and physical structure. We report exceptional bioactive properties that should be used for tissue engineering and tissue regeneration.

COLL 321 Rheology of physically crosslinked networks with junctions of variable multiplicity

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Viscoelastic properties of physical gels whose junctions are formed by the clustering of an arbitrary number of associative groups on polymer chains are theoretically studied by extending the transient network theory originally developed by Tanaka and Edwards. In equilibrium states, the present theory satisfies the equilibrium condition $\Psi_k = K_k \Psi_1^k$ (Ψ_k is the volume fraction of associative groups belonging to junctions with the aggregation number k; K_k is the reaction constant), which agrees with the result obtained from the theory of associating polymer solutions by Tanaka and Stockmayer. It is also shown that the present theory coincides with Tanaka-Edwards theory when each junction takes infinite aggregation number. In this work, we focus on linear viscoelasticity of such physically cross-linked networks and the result is compared with the observed one for associating polymers.

COLL 322 Interfacial behavior of poly(ethylene oxide)-*b*-poly(ε-caprolactone) copolymers at the air-water interface

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The self-assembly of Poly(ethylene oxide)-*b*-Poly(ε-caprolactone) linear copolymers (PEO-*b*-PCL) was studied at the air-water interface. All the polymers have the same PEO chain length (60 repeat units) and the number of ε-caprolactone repeat units in the PCL block ranges from 11 to 35. The Langmuir monolayers were analyzed by surface pressure-mean molecular area (π-MMA) isotherms and compression-expansion hysteresis experiments. The π-MMA isotherms exhibited 3 phase transitions around 6, 11 and 14mN/m. The first 2 transitions at lower pressures are thought to arise from PEO dissolution in the water subphase whereas the higher pressure transition arises from PCL desorption and subsequent crystallization above the interface. The Langmuir-Blodgett films morphologies were also investigated by Atomic Force Microscopy (AFM). AFM imaging revealed formation of crystalline domains in the whole surface pressure range, suggesting that additional PCL crystallization takes place in the monolayer during and after transfer.

COLL 323 New non-ionic block amphiphiles

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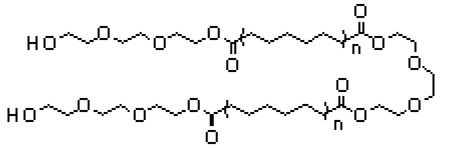
Poly ethylene glycols (PEGs) have been widely utilized in such areas as surfactants, ion-conducting materials, and drug delivery etc. Herein we report that neutral “block” amphiphiles comprised of PEG units and linear alkyl segments in an ABABA pattern have been synthesized using esters as linkers. The molecules have been characterized and their colloidal properties such as surface tension and critical micelle concentration are being examined.



COLL 324 Synthesis and characterization of amphiphilic linear multiblock copolymers

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Amphiphilic linear multiblock copolymers based on 2-(dimethylamino)ethyl methacrylate (DMAEMA) and methyl methacrylate (MMA) were synthesized using group transfer polymerization. All multiblock copolymers were characterized by gel permeation chromatography and proton nuclear magnetic resonance spectroscopy. In particular, the synthesized polymers were the homopolymer of DMAEMA, the diblock of DMAEMA and MMA, the ABA triblock etc, until the ABABABA heptablock copolymer. All DMAEMA blocks had degree of polymerization (DP) equal to 20 and all MMA blocks had DP equal to 10.The hydrodynamic diameters of aqueous solutions of all polymers were determined by dynamic light scattering. The critical micelle concentration of all polymers, was calculated using surface tension, UV-spectroscopy and fluorescence spectroscopy. All polymers were also characterized by small angle neutron scattering. The cloud points of aqueous solutions of the polymers were determined using turbidimetry and the pK of the DMAEMA units were measured by hydrogen ion titration of aqueous polymers solutions.

COLL 325 Sum frequency spectroscopy of block-copolymers at air-liquid and liquid-solid interfaces

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Poloxamers and poloxamines (e.g. Pluronic and Tetronic) are poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide, PEO-PPO-PEO) block copolymers that are widely used in personal care products, separations, pharmaceutical and biomedical applications. In these applications the interfacial properties of the polymers are critical in determining their function and utility.

We describe experiments using IR+Visible Sum Frequency Generation (SFG) spectroscopy to study the structural behavior of poloxamers and poloxamines at the air-liquid interface and liquid-solid interface. SFG is a non-linear surface specific spectroscopic technique that allows non-destructive analysis of the surface of a sample in air. The surface vibrational spectrum was obtained by overlapping a tunable infra red (IR) and visible picosecond laser beam at the interface of the semiconductor. The spectra were obtained by tuning the IR beam over the relevant resonant vibrational modes and measuring the intensity of the reflected sum frequency (SF) beam as a function of IR frequency. The structure of the polymers at the air-liquid interface (as determined by SFG) varies as a function of bulk concentration and bulk additives and these results will be described. We will also describe the molecular structure of the block copolymers at air-solid interfaces.

COLL 326 Surface characterization of diblock copolymers containing poly(ethylene oxide) and various hydrophobic moieties

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A variety of diblock copolymers in which one block is poly(ethylene oxide) (PEO) and the other either poly(vinyl phenylene) (PVP), poly(lauryl methacrylate) (PLMA), or a hydrophobic moiety consisting of alkyl benzyl groups was investigated. Chloroform solutions of the polymers were spread at the air/water interface and characterized as two-dimensional Langmuir monolayers. In addition, the films were transferred onto silicon substrates and the self-assembled patterns examined as a function of solution concentration and mean molecular area as Langmuir-Blodgett films through atomic force microscopy (AFM). The critical micelle concentraion for each polymer was also investigated using dynamic light scattering (DLS). These polymers differ from previous linear coil-coil systems we have successfully modeled; we can thus examine the role of different hydrophobic block geometries and spring constants on the pattern formation. Combining these results provides an experimental basis for the theoretical model of the parameters that control the two-dimensional features.

COLL 327 Direct force balance method for AFM lateral force calibration

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A new and simple calibration method for atomic force microscopy (AFM) is developed. This non-scanning method is based on direct force balances on surfaces with known slopes. The lateral force calibration is performed during force-distance measurements for normal force calibration. This method requires a substrate with known slopes, the z-motion of the piezo calibrated, and the normal spring constant known. This technique determines not only the lateral detector sensitivity (N/V) but also the detector off-set (V/m) and off-centering angle (ɑ) for asymmetric cantilever-tip geometries. Because it is non-scanning, the AFM cantilever can be calibrated without dulling the tip.

COLL 328 Tribochemical interactions between metallic tribosurfaces and triboadditives in view of Lewis acid-base reaction chemistry

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Abstract: Electroneutral or electropositive tribosurface elements as heavy metal Lewis acids and electronegative triboadditive elements as lobe-HOMO Lewis bases were characterized and their tribochemical reactions viewed as inorganic coordination chemistry were mapped on to the Type 23 cell in the Lewis acid/base reaction chemistry matrix. With these characterizations, two experimental tribochemistry cases were analyzed. It was indicated that the interactions between d-block metallic tribosurface elements and p-block lobe-HOMO triboadditive elements in the tribochemical process, including adsorptions and reactions, can be well accounted for by the Lewis acid-base reaction chemistry and the Pearson-Klopman HSAB principle. One tribochemodesign principle concerning the interaction chemistry between metallic tribosurfaces and non-metallic triboadditives was deduced.

Keywords: Metallic tribosurfaces; Triboadditives; Tribochemical interaction; Tribochemistry; Lewis acid-base reaction chemistry.

COLL 329 A Colorimetric Sensor Array for the detection of cadmium using nanostructured cage materials

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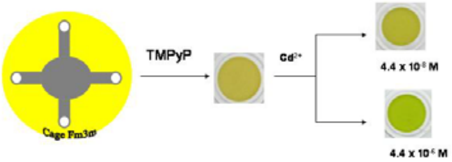
The applicability of monolith cage silica for the development of high sensitive, low cost, simple optical sensor for the visual detection of toxic ions was studied and in this process an optical sensor for the visual detection of cadmium was developed by electrostatic interaction of TMPyP on the cage silica via mercaptopropyl trimethoxy silane. The detection is based on the charge transfer complexation of TMPyP with Cd2+ by changing its color from light orange to green with a bathochromic shift in wavelength to 453 nm from its free ligand band, 429 nm. The intensity of the complex band varies linearly with the Cd2+ concentration in the range of 1.8 × 10-8 to 8.8 x 10-7 mol dm-3, followed which saturation effects were observed. The observed detection and quantification limit of the method was 1.35 x 10-8 and 4.51 x 10-8 mol dm-3, respectively. Factors such as effect of pH, material weight, sample volume and the presence of other ions on the detection method are discussed. The developed sensor shows excellent sensitivity, reusability and kinetically fast, and applied for the analysis of various environmental samples.



Reaction of Cage-TMPyP with different concentrations of Cd(II)

COLL 330 An acid-base analysis on propane oxidation dehydrogenation (ODH) on molybdenum oxide

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The selective oxidation reaction (SOR) of light alkanes is thought as one of the important reactions in the heterogeneous catalysis as the light alkanes available in the abundant nature gas resources is an alternative of petroleum energy sources in the near future, and the key to SOR is the molecular design of oxide catalysts. In this work, we use propane ODH into propylene as the probe reaction to investigate the acid-base effect on the catalytic behavior of molybdenum oxide with semi-empirical methods. Our results show that the activity of catalyst seems to have some “volcano-shaped” relation with its acid, and the selectivity of catalyst does not have any obvious relations with its acid strength. However, the selectivity of catalyst is linearly relevant to the hardness of catalyst, and then we did some fronted-orbital and its corresponding energy analysis with simple model of molybdenum oxide under the density functional theory (DFT) in attempt to correlate the aforementioned results.

COLL 331 Influence of boehmite precursor morphology on gamma-to-theta alumina transformation pathways

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Alumina, in its various forms, is widely used in many applications, including ceramics and catalyst supports. Thermal transformation pathways of alumina have been the subject of numerous studies and are generally well understood. It is widely accepted that when starting with boehmite precursor, the alumina transformation pathway involves gamma-, delta-, theta- and alpha-alumina sequence. Since delta-alumina is not always observed in the transformation sequence, and a new member of the sequence, gamma', has been recently reported, gamma- to theta-alumina transformation has been reexamined in detail. Using hydrothermally grown boehmite precursors with a variety of morphologies, we do not find sufficient evidence that gamma'-alumina exists as a distinct crystalline phase. We find that the presence of delta-alumina in the transformation sequence is strongly influenced by crystallinity of the precursor boehmite. Generally, the larger the boehmite crystallites, the higher the likelihood of delta-alumina occurrence in the transformation sequence.

COLL 332 Magnetic nanoparticle-supported recyclable Pd catalysts

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Magnetic nanoparticles have been employed as novel matrices for supporting homogeneous catalysis. Our group has recently examined the use of maghemite nanoparticle-supported Pd catalysts in promoting Heck, Sonogashira, and Suzuki cross-coupling reactions. These catalysts could be magnetically recovered for repeated uses in the same or different types of reactions. In addition, our recent experiments have found an unusual rate enhancement of our nano-catalysts over their un-supported Pd counterparts in solution. Such rate increases might be due to the unique surface structure of our nano-carriers.

COLL 333 Non-thermal plasma assisted Ag/USY catalyst for NO reduction with C3H6

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Non-thermal plasma-assisted selective catalytic reduction of NOX (SCR) over ultrastable Y zeolite (USY)-based catalysts (Ag/USY, In/USY, Ba/USY were investigated. The USY-based catalysts were almost inactive in thermal SCR, whereas they showed about 50% maximum NOX conversion in NTP-assisted SCR around 150 °C. It was found that the assistance of NTP strongly promoted the NOX adsorption and formation of surface nitrates over USY catalysts. However, introducing NO2 as source of NOX in the reaction gas inhibited the activity, which suggested that NO2 reduction to NO was predominant under this condition. N-containing organic intermediates, which mainly resulted from the activation of propene in NTP, were essential for obtaining high activities at low temperatures. However, it was found that the proportions of key organic species and surface nitrates were also very important to SCR activity. An excess of surface nitrates might result in the reduction of nitrates to NO instead of N2.

COLL 334 Preparation and characterization of nano-particulate CexGd1-xOy solid solutions

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A series of CexGd1-xOy solid solutions were prepared by modified as well as conventional citrate Sol-Gel methods. The structures of the solid solutions were characterized by XRD and Raman spectroscopy. Experiment results show that the solid solutions prepared by modified citrate Sol-Gel method have smaller particle sizes than the samples prepared by conventional method. The CexGd1-xOy solid solutions in face-centered cubic phase are well crystallized in high content of Ce. The particle sizes of solid solutions are obviously smaller than pure Gd2O3 and CeO2, which indicates that the insertion of Gd atoms into the ceria lattice could enhance the thermal stability of the solid solutions. The broad vibration bands around 586 cm-1 are attributed to lattice defects resulting in oxygen vacancies. This indicates that the CexGd1-xOy solid solutions can promote the formation of oxygen vacancies.

COLL 335 Study on oxidation kinetics of calcium sulfite catalyzed by acidum peroxyaceticum

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It was firstly brought forward to add acidum peroxyaceticum as additive into the oxidation system of calcium sulfite in wet limestone scrubbing. The catalyzed effect on formation of sulfate was experimentally studied under heterogeneous conditions. Compared with the results of uncatalyzed oxidation, mechanism about oxidation of calcium sulfite catalyzed by acidum peroxyaceticum was discussed by varying PH, concentration of calcium sulfite, oxygen partial pressure, concentration of acidum peroxyaceticum and temperature. The kinetic model of reaction was established by assumption, which was consistent with the experimental data. It was thought that the general oxidation reaction was controlled by mass-transfer of oxygen under uncatalyzed conditions and by free radicals chemical reaction catalyzed by acidum peroxyaceticum. Thus, the theory was provided for design of the controlling oxidation technics.

COLL 336 Preparation of nitrogen doped nanostructured TiO_2, applications to photocatalytic disinfection

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Nitrogen doped TiO_2 was prepared by a sol-gel method utilizing $Ti(i\text{-}OCH(CH_3)_2)_4$, ammonium hydroxide and urea followed by careful calcining at 400°C to produce predominately an anatase phase of nitrogen doped TiO_2. The TiON produced in this fashion has been characterized by Raman spectroscopy, X-ray powder diffraction, diffuse reflectance UV-VIS spectroscopy, BET surface area, and by dynamic light scattering to measure TiON particle size and particle size distribution.

Bactericidal activity of 5 mg/mL doped TiO_2 suspensions were tested by counting viable cells CFU (colony forming units) after TiO_2 treatment under visible and UV light. Zone of inhibition studies were also carried out after dropping TiO_2 suspensions over a lawn of bacteria on an agar plate followed by treatment with visible and UV light. Results of the synthesis and bactericidal activity will be reported.

COLL 337 Rhodium-phosphine complex supported on MCM-41 for isobutene hydroformylation to isovaleraldehyde

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Isobutene hydroformylation to isovaleraldehyde is very interesting because the product is widely used in many fields. Among Rh-based catalysts, the homogenous catalysts are difficult to be recovered from products, as the result, the supported catalysts become popular. The MCM-41 was synthesized by hydrothermal method. The experimental results revealed that the supported MCM-41 exhibited significant enhancements in the catalytic performances compared with those of catalysts supported by HF-SiO2, ZSM-5 and â-zeolite. The isobutene conversion of HRh(CO)(PPh3)3/HPA-MCM-41 achieved 35.09%, which was twice of the value of HRh(CO)(PPh3)3 /MCM-41. The selectivity of isovaleraldehyde and ASTY value were 96.65% and 208.17 mol/mol, by contrast, a HRh(CO)(PPh3)3 /MCM-41 catalyst presented 48.25% selectivity of isovaleraldehyde and only 54.17 mol/mol ASTF. HPA was very promoting for enhancing the selectivity and activity of the MCM-41 supported Rh catalyst in the isobutene hydroformylation to isovaleraldehyde, which was evident through FT-IR, XRD and N2 adsorption measurements.

COLL 338 Studies on properties of ZrO_2 synthesized by different methods and support effect on methane reforming with carbon dioxide

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Three methods were used to synthesize the zirconia dioxide, including co-precipitation method (marked as ZrO_2-CP), ethonal thermal method(marked as ZrO_2-ET) and solid-state method(marked as ZrO_2-S) as supports for methane reforming with carbon dioxide. The reforming results showed that the methane conversion on different catalysts was increased as: Ni/ZrO_2-CP(53%) < Ni/ZrO_2-ET(71%) < Ni/ZrO_2-S(76%) and during the 6h reaction Ni/ZrO_2-S catalyst exhibited the best stability and good carbon resistance ability. Ni/ZrO_2-S catalysts exhibited excellent reaction performance attributed to its nanosize-effect and good structural properties ¨Cwith large BET surface area(133m^2/g), narrow pore size distribution(5nm) and uniform particle size.

COLL 339 Study on phases and properties of Pr-ZrO2 nanometer material by sol-gel method

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Characterization for Pr-doped Zirconia system prepared by improved Sol-Gel method was performed by means of Raman, XRD, TPR, BET, TG-DSC. It is found that the grain size of the material is 29.1-4.1 nm. Improved Sol-Gel method is an ideal preparative method of nanometer materials. With higher Pr content, the symmetry of t-ZrO2 structure is enhanced and finally the tetragonal phase transforms to the cubic phase. The phase analysis results obtained by laser Raman spectroscopy are not consistent with that obtained by XRD, which indicates that the surface composition is different from the composition of the bulk of the material. The surface region is more easily to form low symmetry phases and can observe a great deal of disorder structure.

COLL 340 The difference ZSM-5 from various synthesis system and their catalytic performances

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ZSM-5 zeolites with similar Si/Al ratio were synthesized successfully using various templates (n-butylamine (BTA), tetrapropylammonium bromide (TPABr) and no template (NT)) under hydrothermal conditions. The samples were characterized by XRD, IR and BET surface area measurements in order to understand the template effects and the differences of the ZSM-5 samples. Toluene disproportionation reaction was carried out over the samples to evaluate the catalytic properties. The results shown that large crystals which have a correspondingly small external surface showed a high para-selectivity, the amount of C9+ and C5-was much less than that of small crystals.

COLL 341 Catalytic reactions of cyclic C_6 hydrocarbons on platinum single crystal studied by sum frequency generation vibrational spectroscopy

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The reactions of C_6 hydrocarbons on platinum single crystals were studied using sum frequency generation (SFG) vibrational spectroscopy and kinetic measurements over a range of pressures (10^{-8}-15 Torr) and temperatures (300 – 500 K). SFG is a surface specific technique that directly probes the surface adsorbates without signal contribution arising from background gases. High pressures of benzene (5 Torr) on Pt(111) formed both chemisorbed and physisorbed benzene at room temperature. Evacuation of the reactant gas after heating to 440 K results in an adsorbed hydrogenated benzene species that appears to be cyclohexyl (C_6H_{11}) or 1,3,5-trihydrobenzene (C_6H_9). Cyclohexene adsorption on Pt(111) at 1.5 Torr in the presence of excess H_2 produces 1,3- and 1,4-cyclohexadiene and π–allyl c-C_6H_9. On the Pt(100) surface only 1,4-cyclohexadiene and π–allyl c-C_6H_9 are observed.

COLL 342 Combined high pressure STM surface structure and reaction rate studies of cyclohexene hydrogenation/dehydrogenation and H2/D2 exchange and their poisoning by carbon monoxide on the Pt(111) crystal surface

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Using high-pressure scanning tunneling microscopy and mass spectrometry, we studied cyclohexene hydrogenation and dehydrogenation reactions and H2/D2 exchange on platinum(111) and their poisoning with CO. We found that during cyclohexene hydrogenation/ dehydrogenation at 298K the surface is disordered, indicating high mobility of the adsorbed species. Introduction of carbon monoxide orders the surface and stops the reaction. When the experiment was performed at 353K the same results were obtained until introduction of CO, which caused the reaction to stop. However STM still revealed a disordered surface. Performing a similar experiment using deuterium instead of cyclohexene we find that H2/D2 exchange occurs until addition of CO at 353K. At this point the H2/D2 exchange continues but at a much slower rate. We propose that the surface is nearly saturated with CO and that the few vacancies existing are mobile enough to generate vacancy aggregates that are large enough to permit H2/D2 exchange but not cyclohexene hydrogenation/dehydrogenation.

COLL 343 Reactions of NO and CO on Pt and Rh bimetallic nanoclusters supported by $TiO_2(110)$

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The catalytic reactivities of NO and CO on mono- and bimetallic Pt and Rh clusters supported on a TiO_2(110) surface were studied using temperature programmed desorption (TPD), scanning tunneling microscopy (STM), low energy ion scattering (LEIS), and x-ray photoelectron spectroscopy (XPS). In CO TPD experiments, CO dissociated on Rh and Pt-Rh nanoparticles, shown by a high-temperature recombinative desorption peak, but CO did not dissociate on pure Pt nanoparticles. In NO TPD experiments, NO dissociated on all the surfaces to form N_2, but no O_2 was observed. In NO + CO TPD experiments, NO and CO preferentially adsorbed on Rh and Pt, respectively, with the result that neither pure metal produced significant amounts of CO_2. However, the bimetallic surfaces showed significant N_2 and CO_2 production, suggesting that the bimetallic nanoparticles have enhanced catalytic activity compared to the monometallic nanoparticles due to increased coadsorption of NO and CO on the bimetallic nanoparticles.

COLL 344 Multifunctional polymeric nanoparticles for photodynamic therapy and nonviral gene delivery

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Nanomedicine is an emerging area that utilizes nanoscale materials for bioimaging, biosensing, diagnostic and targeted therapy[1]. Formulating the nanoparticles composition and functionalizing their surfaces have enabled us to tailor the properties of the nanoparticles for sensing, real time monitoring of cellular interactions, and targeted drug delivery as well as for lighted activated therapy. The talk will provide examples of our efforts in designing multifunctional nanoparticles for nanomedicine. Specifically, applications to photodynamic therapy and gene therapy will be discussed. The talk will conclude with a discussion of emerging opportunities in this field.

1. P.N.Prasad, “Introduction to Biophotonics”, Wiley Interscience, New York (2003).

COLL 345 Active plasmonics: Light emission, modulation and sensing in metal/dielectric nanostructures

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Subwavelength spatial confinement of light at dimensions down to less than 10% of the free-space wavelength is possible using plasmonic components. Ultimately it may be possible to employ plasmonic components to form the building blocks of a chip-based optical device technology that is scaleable to molecular dimensions, with potential imaging, spectroscopy and interconnection applications in computing, communication and chemical/biological detection. In this talk I will describe recent opportunities presented by plasmonics for chip-scale integration of photonic and electronic devices, including i) plasmon-enhanced emission from quantum dots, and ii) plamon-mediated electro-optic and all-optical modulation of optical transmission through subwavelength hole arrays and iii) strategies for in-coupling and out-coupling of light plasmonic devices.

COLL 346 Strategies for the design of plasmonically coupled nanoparticle assemblies

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Multi-component plasmonic nanostructures have tunable resonances that depend sensitively upon configuration and upon the dielectric properties of material assembled in the interparticle regions. While these sensitivities have the potential to endow coupled plasmonic nanostructures with value as dynamic optical filters or addressable substrates for molecular detection, they simultaneously impose stringent requirements for homogeneity among assemblies destined for applications that depend upon the reproducibility of their optical properties. While either lithography or solution phase self-assembly can be used to construct coupled nanostructures, the structural control required for predictable plasmonic performance is difficult to achieve when either technique is used alone. An alternative fabrication strategy that incorporates both top-down and self-assembly methods is introduced. The hybrid method circumvents some of the problems inherent to the strategies that rely on patterning or self-assembly, alone, and may have the potential to provide the structural control required to generate arrays of multi-component assemblies with dynamically controllable plasmonic properties.

COLL 347 Shape controlled nanostructures for improved LSPR based biosensors

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The significant potential of localised surface plasmon resonances at metallic nanoparticles as a high sensitivity route to detection of molecular binding events has lead to significant recent research focus. The plasmon resonance properties can be tuned via changes in the nanoparticle material and geometry and the control of shape of nanoparticles can lead to improved biosensor systems. Nanoparticle disks, holes (in thin metal films) and rings prepared via a colloidal lithographic route have been studied as potential substrates for LSPR based biosensing. Shape changes correlate to changes in both resonance energy and refractive index sensitivity with similar behaviour for disk and holes. However ring structures exhibit resonances in the near infrared with significantly higher sensitivities (&gt600 nm/R.I. unit) compared to disk/hole structures of a similar size or resonance energy. Detection of molecular binding events to specific parts of the structures are demonstrated.

COLL 348 Advanced surface modifications of gold films with nanoscale holes for optimized and quantitative label-free plasmonic sensing

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In analogy to colloidal particles made from noble metals, nanoscale holes in thin noble metal films display localized surface plasmon (LSPR) behavior. In the strive for new label-free affinity-based bioanalytical sensors, the fact that the color associated with LSPR active substrates is sensitive to changes in the interfacial refractive index has made the concept promising for array-based sensing. While the highest sensitivity was so far demonstrated for discrete nanoscale features of noble metals, hole-containing substrates have the advantage of being conductive. This, in turn, open up a convenient means to combine the LSPR sensing concept with alternative analytical approaches, here proven by letting such a substrate act as working electrode of a quartz crystal microbalance sensor - enabling a convenient way to simultaneously probe changes in frequency (Δf), energy dissipation (ΔD) and changes in peak position ($\Delta\lambda$). This, in turn, provides a novel means of comparing dynamic mass (including hydrodynamically coupled water) and optical mass (proportional to changes in interfacial refractive index), while independently allow for a quantification of the LSPR response, for which detailed theoretical descriptions are yet to be fully developed. Emphasis will also be put on advanced means of selectively modifying either the bottom of the holes (composed of e.g. SiO_2, TiO_2 or ITO) and the planar metal substrate (e.g. Au, Ag or Pt) to direct biorecognition reactions selectively to predefined nanoscale regions.

COLL 349 Optical and X-ray scattering studies of DNA-directed nanocrystal groupings

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This talk will describe recent work in which we have investigated discrete groupings of nanocrystals assembled using nucleic acids. In the case of metal nanocrystals with strong plasmon light scattering spectra, coupling between the plasmons leads to a unique spectrum for each arrangement of

nanocrystals. This means that the scattering spectra can be used as spectroscopic probes. Further, Small Angle X-ray Scattering spectra are also very sensitive to the arrangement of nanocrystals, and can provide an additional calibration of the plasmon spectroscopic ruler.

COLL 350 First ten angstroms at the National Science Foundation

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A number of recent advances have impacted the surface chemistry portfolio at the NSF. The nano revolution has brought new aspects to modern surface chemistry. Friendlier environments in surface instruments have enabled inquiries into interfacial phenomena relevant to biology and earth sciences. Higher computing power has enabled better theory supporting surface chemistry. Improved communication has enabled more international collaboration. This talk will review some of the themes and tensions affecting research in surface chemistry at the NSF Division of Chemistry.

COLL 351 Growth and properties of gold nanoarrays

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Vapor deposition of small quantities of gold onto highly ordered pyrolytic graphite (HOPG) can be used to generate a wide range of interesting nanostructure arrays. The specifics of the nanostructures that are generated can be varied by controlling the temperature of the HOPG during deposition. Deposition onto a room temperature substrate results in the growth of dendritic islands. Higher substrate temperatures generates gold nanodots decorating graphite steps, leading to large arrays of parallel “beaded” (non-continuous) gold nanowires. Data on the optical properties of arrays of parallel beaded gold nanowires will be presented and discussed. The use of arrays of “beaded” gold nanowires on HOPG as electrodes for subsequent electrochemical metal deposition to form continuous metal nanowires will be presented.

COLL 352 High-resolution scanning probe microscopy of optically-resonant atomically-flat nanoparticle substrates

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We demonstrate molecularly-resolved scanning tunneling microscopy (STM) of self assembled monolayers (SAMs) on flat gold nanoparticles (FGNPs) supported on indium tin oxide (ITO) coated glass. The FGNPs are atomically-flat single crystals with large {111} surfaces which expose only 3-4 atomic layers. These novel substrates are simple and inexpensive to prepare. They have the added advantage over conventional Au{111} substrates (bulk single crystals and Au thin films on mica) that they are also optically-resonant plasmonic antenna. We have also imaged the plasmon mode structure of FGNPs using spectrally resolving white-light scanning near-field optical microscopy (NSOM).

COLL 353 Probing crystal surfaces at the near molecular level

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Advances in atomic force microscopy (AFM) now permit real-time in situ exploration of crystal surfaces at the nanoscale, including analysis of epitaxial relationships between films and substrates, visualization of thin film growth, molecular adsorption on crystal surfaces, crystal surface morphology, determination of rudimentary crystal structure, and crystal growth processes, often under conditions of practical as well as fundamental interest. More recently, AFM has been used to to measure adhesion forces at crystal surfaces at the molecular level. This presentation will highlight some recent advances pertaining to these capabilities, with particular emphasis on epitaxial growth of crystalline organic films and growth and adhesion of crystalline biomineral surfaces.

COLL 354 Copper clusters formed on the Si(111)-(7×7) surface via molecular anchor

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Nanostructures on surfaces have been receiving much attention due to the intrinsic interest in structures with reduced dimensions as well as their potential technological applications. Self-assembled nanostructures are expected to have smaller sizes and stronger confinement potentials compared to the lithographically defined features. We report the formation of copper clusters on a thiophene mediated Si(111)-(7×7) surface studied using a scanning tunneling microscope (STM). Thiophene selectively binds to the adjacent adatom-rest atom pair on the Si(111)-(7×7) surface, leading to the covalent attachment of C-S-C linkages onto the surface, which can act as molecular anchors for attaching other metal atoms. Cu-atoms were found to preferentially adsorb onto the S-atoms of the functional C-S-C groups in the formation of copper nanoclusters on the thiophene-mediated Si(111)-(7×7) surface. ACKNOWLEDGMENTS. Y. P. Zhang acknowledges the financial support by the Singapore Millennium Foundation.

COLL 355 Structure sensitivity in CO oxidation and NH3 decomposition

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Clean Ir catalytic surfaces are prepared reversibly from the same crystal in situ with different surface morphologies, from planar to nanoscale pyramidal structures with (110) and {311} facets of various sizes. Both CO oxidation and NH3 decomposition are structure sensitive on clean planar Ir(210) versus clean faceted Ir(210). At low oxygen pre-coverages, the temperature Ti for the onset of CO2 desorption decreases with increasing CO coverage. At high oxygen pre-coverages, Ti is <330K, and independent of CO coverage. No evidence has been found for size effects in CO oxidation over faceted Ir(210) for average facet size ranging from 5nm to 14nm. In contrast, NH3 decomposition on faceted Ir(210) exhibits nanoscale size effects; this is the first report of size effects in surface chemistry on an unsupported monometallic catalyst with well-defined structure and controlled size. This work has relevance to air pollution reduction for environmental applications and carbon-free H2 production for fuel cell applications.

COLL 356 Polymorphism in solutions of amphiphilic polymer globules

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To simulate amphiphilic polymers, we introduce an extended hydrophobic/hydrophilic (HP) model, which incorporates the dualistic nature of monomer units, each consisting of hydrophobic (H) and hydrophilic (P) interaction sites. The hydrophobically-driven conformational transitions are studied using MD simulations. We find that, depending on the interaction between H and P sites, a variety of

thermodynamically stable anisometric chain morphologies are possible in a solvent selectively poor for H sites, including disk-like structures, stretched strings of intramolecular micelles, and cylindrical-shaped conformations. Amphiphilic polymers with semiflexible hydrophobic backbone demonstrate even more complex conformational behavior. In this case, we observe the formation of compact conformations resembling a collagen-like structure in which the semiflexible chain folds itself a few times and different strands wound round each other. The collagen-like structure can coexist with toroidal globules.

COLL 357 Self-association of block polyampholytes

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Regimes of electrostatic self-association between oppositely charged polymers are analyzed by scaling theory and computer simulations using an example of block polyampholytes. Electrostatically-driven coil-to-globule transition of a symmetric diblock polyampholyte is investigated with three regimes identified with increasing interaction strength: folding, weak fluctuation-induced, and strong binding regimes. Similar weak and strong electrostatic associations are predicted for cores of block polyampholyte micelles and for complexes of oppositely charged polyelectrolytes. Electrostatic association in solutions of asymmetric diblock polyampholytes leads to the formation of stable spherical micelles. The cores of these micelles, formed by oppositely charged blocks, are stabilized by the coronas of higher charged blocks. Even monodisperse asymmetric block polyampholytes self-organize into two populations inside the micelle. One group of chains keeps both blocks entirely in the core. The chains in the other group localize the lower charged block in the core, while the higher charged block is entirely in the corona.

COLL 358 Micellization and colloidal adsorption of a model polyelectrolyte diblock copolymer in selective solvent: Theoretical model combining scaling and lattice mean field approaches

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New theoretical model based on scaling and lattice mean-field approaches is formulated and implemented, for describing competitive micellization and adsorption of linear polyelectrolyte diblock copolymers onto flat colloidal particles in selective solvents. This model describes some practical situations in colloid science. Previous investigations have generally looked at non-electrolyte block copolymers in such a scenario by scaling theory or alternatively by molecular level lattice Monte-Carlo simulations. The motivation for our work is the powerful ability of scaling and mean-field methods to address physical behavior of complex fluids containing chain molecules over multiple length scales. We study situations where the electrolyte block forms micelle corona and the neutral block comprises the core. For the adsorption onto colloidal surface, the electroyte block is non-adsorbing while the neutral block is adsorbing. Micellar thermodynamic descriptions provided by Shusharina et al., are used with some corrective modifications. The adsorption onto colloid surface is modeled by Scheutjens-Fleer mean-field theory for adsorbing block. For electrolyte segments in good solvent (aqueous), the osmotic regime is invoked in the brush state, with osmotic and elastic stretching terms formulated in the most self-consistent manner. The dilute case, planar brush and spherical brush for the micelle corona, and the dilute and concentration cases for adsorption onto colloid were studied with appropriate formalisms for each block. Variation of micellization and adsorption free energies, under equilibrium thermodynamic conditions, regimes of micellization/adsorption are studied with respect to block lengths and charge {na, nb and t}.

Extension of this model to include adsorption on spherical colloidal particle surfaces and interparticle interactions (colloidal stabilization) will also be presented.

COLL 359 New necklace model of hydrophobic polyelectrolytes

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We have developed a necklace model of hydrophobic polyelectrolytes in which the necklace structure appears as a result of the counterion condensation and is caused by the balance of the correlation-induced attraction of condensed counterions to charged monomers and electrostatic repulsion between uncompensated charges. The size of the beads increases with polymer concentration while their number per chain decreases. The model predicts coexistence of necklaces with different number of beads on a polymer backbone at any polymer concentration. To test this necklace model we performed molecular dynamics simulations of polyelectrolyte chains with a degree of polymerization N varying from 25 to 373 and with fraction of charged monomers f=1/3, 1/2 and 1 in poor solvent conditions for the polymer backbone. The observed concentration dependence of the bead size supports the assumption of the counterion condensation origin of the necklace structure. The Kratky plot of the chain form factor is in excellent agreement with the neutron scattering data.

COLL 360 Hydration, Phase separation and shear thickening in solutions of associating polymers

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Aqueous poly(ethylene oxide) (PEO) solutions show closed-loop phase separation region (miscibility loop) at intermediate temperatures, while poly(N-isopropylacrylamide) (PNIPAM) solutions show very flat LCST cloud-point lines which are horizontal up to 20 wt% of the polymer concentration with almost no molecular weight dependence. We theoretically show that phase behavior observed in PNIPAM solutions is caused by the strong correlation between the nearest-neighboring hydrogen-bonded bound water molecules on the polymer chains (cooperative hydration), and compare theoretical phase diagrams with the observed ones. We then study molecular association and thermoreversible gelation of telechelic PEO and PNIPAM. The LCST goes down by end-chain association (association-induced phase separation). Association eventually leads to gelation. Finally, paying special attention to nonlinear stretching of the main-chains, molecular origin of shear thickening in networks with temporal micellar cross-link junctions is studied on the basis of the transient network theory and molecular simulation.

COLL 361 Colloidal phase separation of PNIPAm solutions

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Phase separation with temperature of aqueous PNIPAm polymer solutions are studied up to high concentrations (~6 wt%) by means of neutron and light scattering. In all the accessible range of concentrations and diphasic temperatures, a colloidal phase separation is evidenced. Despite the electrical neutrality of PNIPAm, charged stabilized colloids of PNIPAm rich phase are formed after the quench. The colloidal size is found to decrease with the quench temperature in agreement with a spinodal decomposition scheme which is blocked by the adsorption of charged species at the colloid surface.

COLL 362 Molecular dynamics simulations of amphiphilic dendrimers in solution

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Dendrimers are large, synthetic macromolecules that have regular and highly branched architectures. A dendrimer has a large number of terminal groups that can be functionalized to tune its properties for use in a wide range of applications, including: medicine, surface science, and catalysis. For example, hydrophilic terminal groups can be used to solubilize hydrophobic dendrimers in water to create a unimolecular micelle. We performed molecular dynamics simulations on model amphiphilic dendrimers to better understand the conformational changes that variations in terminal group type and arrangement impart to the dendrimer. We will present simulation results for a dendrimer in dilute solution, where the interior monomers are solvophobic and the terminal monomers are varied systematically from all solvophobic to all solvophilic. We will discuss how the size, shape, and mobility of the dendrimer and its parts change according to the fraction and arrangement of the two types of terminal monomers.

COLL 363 Simulations of polymer solutions in confined geometries

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An efficient method of simulating polymer solutions has been implemented by combining the fluctuating lattice-Boltzmann method with micromechanical models of the polymer molecules. In this algorithm, uncorrelated thermal fluctuations are added to the fluid rather than correlated random forces on the beads. Beads interact with the fluid via a frictional coupling. Therefore, the hydrodynamic interactions between the monomers develop in time and space from purely local interactions and the computation scales linearly with the number and length of the polymers. This approach enables simulation of the dynamics over an unprecedented range of scales – recent work shows that it is feasible to calculate the dynamics of a hydrodynamically interacting polymer with 1024 beads. We demonstrate the capabilities of the technique on some problems of relevance to microfluidic flows, including lateral migration of polymers under confinement and the separation of biopolymers using entropic trapping mechanisms.

COLL 364 Dynamics of confined flowing polymer solutions

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Simulations of non-dilute solutions of polymers confined between two infinite walls are performed for Couette and Poiseuille flow, in order to study the effects of concentration on the confined polymer dynamics. The simulations are done using a bead-spring dumbbell/chain Langevin description of the polymer dynamics and a Green's function technique is used to account for hydrodynamic interactions between dumbbells and perturbations due to wall confinement. The algorithm scales as O(N log N) which enables simulations at finite concentration. A depletion layer significantly larger than the polymer radious of gyration forms during flow, due to the hydrodynamic interactions of the polymers with the walls, in agreement with experimental observations. At finite concentration the increased shear rate near the wall (due to lower concentration) competes with the hydrodynamic screening of the wall by the presence of multiple chains.

COLL 365 Hierarchical modeling of polymers with a non-linear molecular architecture: Calculation of branch point friction and chain reptation time of an H-shaped polyethylene melt from detailed atomistic simulations

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A hierarchical strategy is presented for simulating structure and dynamics in polymers characterized by a non-linear molecular architecture, such as the H-shaped macromolecules. First, a novel Monte Carlo (MC) algorithm, built around state-of-the-art chain connectivity altering moves, like the end-bridging and double-bridging, is employed to generate well equilibrated atomistic configurations of these highly non-linear chain structures. Then, the equilibrated structures are used as initial configurations in detailed NPT MD simulations of H-shaped polyethylene (PE) melts for very long times, on the order of microseconds. In our simulations, the average number of carbon atoms in the backbone has ranged from 48 up to 300 corresponding to both unentangled and entangled crossbars, while the average branch length was kept relatively small (it ranged from 24 up to 50 carbon atoms) corresponding always to unentangled arms. The MD simulation results provide convincing evidence for the different relaxation mechanisms exhibited by an H-polymer melt: the fast relaxation due solely to arm breathing (on the order of a few ns, for an H_300_50 melt), and the slow branch point diffusion which is accompanied by a sluggish backbone diffusion due to reptation (on the order of a few ìs, for an H_300_50 melt). They have further demonstrated that the center-of-mass diffusivity in an H-polymer follows faithfully that of branch points, thus validating from first-principles the main assumption of the McLeish-Larson pom-pom theory that all friction in an H-molecule is concentrated at the branch points.

COLL 366 Mesoscale model of polymer melt structure: Self-consistent mapping of molecular correlations to coarse-grained potentials

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Development and application of coarse-graining methods to condensed phases of macromolecules is an active area of research. Multiscale modeling of polymeric systems using coarse-graining methods presents unique challenges. Here we apply a coarse-graining method that self-consistently maps structural correlations from detailed molecular dynamics (MD) simulations of alkane oligomers onto coarse-grained potentials using a combination of MD and inverse Monte Carlo methods. Once derived, the coarse-grained potentials allow computationally efficient sampling of ensemble of conformations of significantly longer polyethylene chains. Conformational properties derived from coarse-grained simulations are in excellent agreement with experiments. The level of coarse graining provides a control over the balance of computational efficiency and retention of chemical identity of the underlying polymeric system. Challenges to extension and application of this and similar structure-based coarse-graining methods to model dynamics and phase behavior in polymeric systems are briefly discussed.

COLL 367 Analytical rheology: Linear viscoelasticity of model and commercial long-chain-branched polymer melts

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Unlike chromatography and spectroscopy, rheology of branched polymer melts exhibits great sensitivity to both, the numbers and type of long-chain branching, and in principle, it can provide the most accurate characterization. However, quantifying branching information reliably from rheology has been elusive thus far, due to lack of sufficiently accurate theories for complex branched polymers and to the ill-posed problem of fitting rheological data with models of long-chain branching in which there are too many parameters, including the density of branch points, branch lengths, the locations of the branches along the polymer backbone, and the polydispersity of molecular weight. Incorporating mean-field ideas conceived and fleshed out over the years by de Gennes, Doi and coworkers, Marrucci, McLeish, Milner, and others, we present our efforts to produce a “hierarchical algorithm” to predict the relaxation of general mixtures of the branched polymers. We show that the general algorithm can predict accurately the linear rheology of both simple linear and star-branched polymers, and their mixtures, and also lightly branched commercial metallocene polymers. Limitations on the predictive ability of the algorithm for highly branched comb polymers lead us to consider more deeply the problem of branch point motion and primitive path fluctuations using more microscopic simulation methods, including “slip link” models and pearl-necklace molecular dynamics simulations. Results from these recent simulations, and their bearing on the development of a general algorithm for predicting the linear rheology of commercial branched polymers, will be discussed.

COLL 368 Brownian dynamics simulations of rigid and semi-rigid polymer fibers

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Results from Brownian dynamics simulations demonstrate the importance of the choice of hydrodynamic model of rigid polymer fibers upon the behavior of the rotational diffusivities at high concentrations. These simulations demonstrate that the scaling behavior of the rotational diffusivity within the semi-dilute concentration regime depends upon the ratio of short-time rotational (D_{R0}) and average center of mass (D_{T0}) diffusivities. As L^2D_{R0}/D_{T0}, where L is the rod length, varies between 4 (a rigid-dumbbell model) and 9 (a slender-body model) for polymer fibers of high aspect ratio, the scaling of the rotational diffusivity transitions between approximately $D_R/D_{R0}\sim(nL^3)^{-1}$ and $(nL^3)^{-2}$. Therefore, numerical results can capture either of these scaling results, both of which are well-known theoretical predictions. By relaxing the rigid constraint and enabling slight bending of the rods, it is also shown that semi-rigid fibers exhibit a similar dependence of the scaling of the rotational diffusivity on the ratio of short-time rotational and translational diffusivities at sufficiently high concentrations. The flexibility also delays the onset of the semi-dilute concentration regime where the rods are significantly confined and the power-law scaling is observed. After the semi-dilute regime has been entered, the semi-rigid fibers behave similarly to rigid fibers, with power-law scalings that are nearly identical. Results of these simulations provide insight into the modeling of real colloidal systems of rigid, or nearly rigid polymer fibers.

COLL 369 Structure and dynamics of magnetorheological colloids in microfluidic devices

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The characteristic length scales found in microfluidic devices have been shrinking drastically over the past several years. As a result it is becoming increasingly important to study the effects of this tight confinement. We have used the Brownian Dynamics simulation technique to study the self-assembly of magnetorheological (MR) colloids under confinement. To compliment these simulations, we have used particle tracking to study micron-sized colloids assembling in fluidic channels. For quasi-two dimensional systems, we report a seemingly contradictory response of the system to confinement between parallel hard walls. In contrast to previous circular geometries, we see re-entrant melting with respect to changing channel width and not with respect to field strength. As the channel height is increased (in the range of a few particle diameters), we observe oscillations in the mean cluster spacing with respect to gap height. These oscillations and the transition to the large gap scaling regime will be discussed.

COLL 370 Polymers at interfaces: From depletion to association to stabilization of colloids in melts

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The consequences of polymers dissolved in fluid phases and/or adsorbed onto micron or submicron entities for the stability and rheology of the colloidal dispersions poses a theme that has roots in the distant past but continues to pose interesting and fundamental issues for both technologically and biologically important systems. The modern history of the subject on the physical side began with an understanding of depletion attraction that started to emerge in the 1950s and motivated the invention and exploitation of associative polymers beginning in the late 1980s. Only recently has the nature of colloidal interactions when the continuous phase consists of a polymer melt begun to be understood. This talk will trace that history and define the issues to be addressed for polymer melts containing colloidal particles.

COLL 371 Field mediated self assembly and actuation of highly parallel microfluidic devices

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For the practical realization of microscale fluidic devices that mimic the operation of their macroscale counterparts, two significant hurdles must be overcome. The first, fabrication, is currently being addressed through either improvements in the resolution of macroscale techniques (“top down”) or through synthetic chemical approaches to create increasingly complex molecular structures (“bottom up”). Though both approaches have achieved some success, the creation of working devices within their final functioning environments remains difficult. The second hurdle involves the delivery of energy across length scales to effectively power microdevices in a desired and controlled fashion once they have been created. Here we present a bulk-field based in-situ technique that addresses both issues by not only driving device assembly from simple colloidal building blocks but also by subsequently powering the devices in their microenvironments once fabricated.

COLL 372 Streaming potential and streaming current near a rotating disk bearing a thin double layer

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2-D crystallization rates of microscopic particles, driven by a/c electric currents, depend strongly on the species of electrolyte present [Langmuir 21, 1784 (2005)]. For frequencies less than a few hundred Hertz, we believe the chemical specificity arises from the effect of electrode reaction kinetics on changes in zeta potential caused by passing current through the double layer [Colloids Surf. A 250, 67 (2004)]. As a first step toward evaluating the effect of reaction kinetics and current on zeta potential, we performed an experimental and theoretical study of the streaming potential produced by a rotating disk, which is a commonly used by electrochemists in the study of electrode reactions. Although no electric current was imposed in these preliminary experiments, the rotating disk appears to be a promising new device for measurement of zeta potential on flat surfaces.

COLL 373 Diffusive and convective transport of proteins in fibrin gels

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A quantitative understanding of diffusion and convection of proteins and other bio-molecules within gels such as extra-cellular matrix is necessary for estimating drug delivery rates, controlling the temporal and spatial delivery of growth factors for tissue engineering applications, and predicting drug-activated dissolution of thrombus. The objective of our research was the creation of an

experimental system based on fluorescence microscopy to determine transport rates of proteins and water in gels. The proteins were labeled with cyanine dyes, which allowed us to follow the evolution of concentration gradients of the proteins. Results are reported for fibrin gels; specifically we determined 1) the diffusion coefficient of Insulin-like Growth Factor (IGF-1) and Ribonuclease (RNase) in the gels; 2) the hydrodynamic permeability of the gels; and 3) the flow-induced dispersion of RNase in the gels. The gels were 0.4% fibrin and supported in a long (5 cm), thin (200 ƒÝm) rectangular capillary. An important result is the finding that the dispersion coefficient of the protein under flow conditions was 2-3 times greater than the diffusion coefficient of RNase.

COLL 374 Bending colloidal aggregates with light: The micromechanics of particulate gels

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The micromanipulation and dynametrical capabilities of laser tweezers provide the ability to probe the mechanics and interactions of colloidal materials on nanometer to micrometer lengthscales. I will present a recent application of laser tweezers to investigate the mechanical properties and microrheology of particulate gels. Our approach focuses on the micromechanics of aggregates that mimic the stress-bearing backbone in gels. Using time-shared optical traps, backbone mimics are directly assembled in salt solutions into precisely-controlled geometries. The aggregate bending rigidity is then measured. Aggregates behave elastically up to a critical bending moment, after which they exhibit small stick-slip rearrangements. The bending rigidity is found to be sensitive to the particle surface chemistry, ionic species and ionic strength. The bending rigidity between individual particles agrees with the JKR model of particle adhesion, providing a direct link between the micromechanics and the interfacial adhesion energy of the particles. Overall, these experiments enable us to bridge macroscopic rheology of colloidal gels to the underlying microstructural response. Furthermore, the new insight we have gained provides useful strategies for controlling gel behavior by manipulating the nanoscale near-contact interactions between Brownian particles.

COLL 375 Towards synthetic antibody via surface grafting

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Present communication describes an approach to fabrication of a synthetic material capable to recognize a specific protein. In our study pockets have been generated (on a surface) with the orientations and dimensions of a protein. The beds of the cavities have been covered with amino acids grafted to the surface. The walls of the pockets are made of polymer grafted layer, which is attached to the substrate at the locations free of the anchored amino acids. To create the imprinted structures deposition of thin film of poly(glycidyl methacrylate) (PGMA) was used for the initial surface functionalization. Next, adsorption of fibrinogen molecules on the PGMA film was conducted in regimes where complete monolayers of adsorbed proteins were not formed. The remaining space between the adsorbed fibrinogen macromolecules was grafted with end-functionalized polyethylene glycol. At the last stage treatment of the anchored protein/grafted polymer layer with non-selective protease was conducted.

COLL 376 Synthetic and biological hybrid polymers

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Foldable polymers with alternating single strand deoxyribonucleic acid (ssDNA) and planar conjugated organic perylene tetracarboxylic diimide units were found to self-organize into loosely folded nanostructures. Upon heating, the loosely folded structures become more ordered as evidenced by perylene stacking. The folding and unfolding processes driven by the molecular interactions of adjacent perylenes were monitored in both aqueous and organic solutions. Heat-promoted folding, or inverse temperature behavior, which originates from positive enthalpy changes, was only observed in water. Therefore, we attributed this inverse temperature dependence to hydrophobic effects rather than molecular orbital overlap between perylenes. Moreover, the biological sequence provides highly specific molecular recognition properties while the physical properties of synthetic chromophores offer sensitive fluorescence detection. In this report, we describe that rational designed hybrid foldamers exhibit potential in the detection of polynucleotides or proteins. These findings shed light on the design of new thermophiles in protein engineering as well as the construction of macromolecular-based nano-devices with actuator and sensory properties.

COLL 377 Controlling fibronectin and A7r5 adhesion and cell motility using polyelectrolyte multilayers

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Use of polyelectrolyte multilayer thin films (PEMU) allowed the control of adhesion of fibronectin (FN), an extra cellular matrix protein. It also allowed the control of the adhesion and motility of A7r5 rat aortic smooth muscle cells. Optical waveguide lightmode spectroscopy and immunofluorescence localization were used to determine quantitatively and qualitatively the amount of fibronectin bound on each PEMU. FN bound strongly to PEMUs terminated with poly(allylamine hydrochloride) (PAH) or Nafion®. Laser confocal microscopy was used to determine the cell spreading and locomotion. A7r5 cells spread best on Nafion® terminated PEMUs but showed little evidence of locomotion. Cells spread less on PAH terminated PEMUs but showed good motility on this surface, they also left FN trails as they migrated. Poly(acrylic acid)-*co*-poly(3-[2-(acrylamido)-ethyldimethylammonio]propane sulfonate) PAA-*co*-PAEDAPS showed both FN and cell repellency. FN pre-coating on PAH terminated PEMUs increased cell spreading and decreased cell motility; however, no change was observed on Nafion® coated PEMUs

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COLL 378 Responsive thin film membranes from cross-linked polyelectrolyte

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We present the simple route to pH-responsive thin film membranes with submicron pores and switching surfaces on their base. The membranes were fabricated onto flat substrates from a solution of a cationic polyelectrolyte and a cross-linker in humid environment. The presence of water vapor was found to be necessary for the formation of pores. The cross-linked membranes were stable in water and showed pH-dependent swelling, which in turn had a significant impact on the pore size. The membranes were further modified using the layer-by-layer technique to prepare surfaces, which demonstrated unusual wetting behavior.

COLL 379 Chromatic bio-mimetic lipid-polydiacetylene films and vesicles for studying biological recognition

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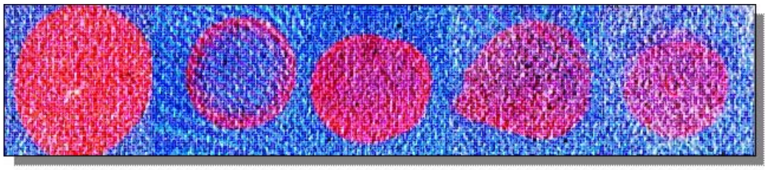
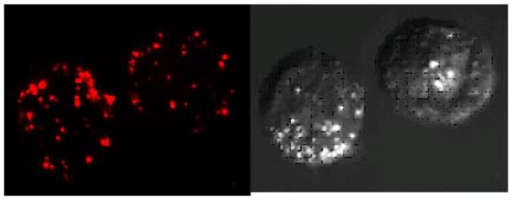
I will describe the creation of new bio-mimetic membrane assemblies composed of phospholipids (the biological recognition platform) and polydiacetylene (color/fluorescence reporter). The interspersed lipid/polymer films and vesicles have been employed for studying varied membrane processes and bio-molecular recognition phenomena. Specifically, we have shown that structural perturbations occurring at the lipid/polymer interface give rise to dramatic blue-red color transitions and induction of fluorescence emission within the polymer domains. Application of the new platform will be described in analysis of drug-membrane interactions, ligand-receptor recognition and the construction of living-cell sensors. Recent references: - “Microscopic visualization of alamethicin

incorporation into model membrane monolayers", Volinsky et al, Langmuir, 2004, 20, 11084-11091. - "Selective detection of catecholamines by synthetic receptors embedded in chromatic polydiacetylene vesicles" Kolusheva et al, J. Am. Chem. Soc., 2005, 127, 10000-10001. - "Visualization of membrane processes in living cells by surface-attached chromatic polymer patches", Orynbayeva et al, Angew. Chem. Intl. Ed., 2005, 44, 1092-1096.





COLL 380 Amplification of biomolecular interactions using peptide substrates of enzymes that are polymerized at interfaces between aqueous phases and thermotropic liquid crystals

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We report a novel method that employs the orientational ordering of liquid crystals to amplify and transduce the activity of enzymes at interfaces. The method involves the polymerization of peptide substrates of enzymes at interfaces between aqueous phases and immiscible liquid crystals. We illustrate the approach using the 17-amino acid peptide substrate that contains residues 187-203 of SNAP-25. This peptide sequence is a substrate for trypsin and botulinum neurotoxin type A. By contacting an aqueous solution of the peptide with the nematic liquid crystal 5CB containing adipoyl chloride, an enzymatically cleavable polymer membrane was generated at the interface between the liquid crystal and aqueous solution. Following incubation of the membrane against trypsin, we observed degradation of the membrane: introduction of a dispersion of vesicles of L-α-dilauroyl phosphatidylcholine (L-DLPC) into the aqueous phase triggered an orientational transition in the liquid crystal. The orientational transition of the liquid crystal was easily observed by the transmission of polarized light through the liquid crystal. In contrast, membranes incubated in aqueous solutions containing α-chymotrypsin or bovine serum albumin (which do not cleave the 17-mer peptide) did not lead to an orientational response of the liquid crystal. Extensions of these principles to detection of botulinum neurotoxin type A (BoNT/A) will also be discussed in this presentation.

COLL 381 Delivering drugs layers at a time: New approaches using electrostatic assembly

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Smart drug delivery — the release of drugs when and where they are needed in the body — is a goal for a number of new technologies that have been introduced recently. We have developed a means of generating ultrathin polymeric films that can contain a broad range of therapeutic drugs that can be placed into specific regions of the film, and then released in inverse sequential or simultaneous order. Here we present two means of generating thin films that can be "programmed" to release specific drug molecules at different times. In the first approach, we utilize a hydrolytically degradable polycation that is alternated with charged macromolecular or sensitive biologic and protein drugs to

generate ultrathin conformal polymeric coatings with compositions controlled on the nanometer length scale to allow complex, tuned drug delivery profiles and the sequential or simultaneous release of multiple drugs. New developments have allowed us to control the order and timing of multiple drug release from the film. The second approach involves the incorporation of redox active species within the layer-by-layer thin film that facilitates the electrochemically induced release of drugs, with control of the rate of release and amount released via the manipulation of electrochemical potential and scan rate. These methods are simple, low cost, and allow infinite tuning of film composition, and subsequent degradation or decomposition under biological conditions to release drugs layers at a time.

COLL 382 Colloidal ordering in nanoparticle, polymeric and biological systems

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The physical and chemical processes governing the behavior of complex fluids result from a delicate balance of molecular forces. In this fine equilibrium, order often prevails. Suspensions of monodisperse, charge-stabilized colloidal particles are useful model systems to study this ordering. Numerous groups have noted the bright iridescence from colloidal crystals, such as opals, diffracting visible light. Analogous ordering also occurs in suspensions of polymeric micelles and in two-dimensional arrays of proteins. In this lecture we will review the diversity of systems undergoing disorder-to-order transitions and highlight the similarities and differences between the crystallization processes. Such phenomena were long of interest as tests of theory and as curious structures sometimes found in nature. Now there are several examples where colloidal ordering is central to the creation of important new materials or devices.

COLL 383 Structure and reactivity in organic monolayers

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Organic monolayers can be formed by physisorption of long-chain hydrocarbons parallel to the substrate, or by chemisorption of long-chain organics upright on the surface. We will discuss our recent work examining the structure, composition, and reactivity of several of these monolayer systems, which serve as important models with some relevance to molecular electronic devices, surface modification for biocompatibility, molecular recognition, tribological and corrosion inhibition systems.

The physisorption of long-chain alkane and substituted long-chain alkane molecules at the basal plane of highly oriented pyrolytic graphite (HOPG) results in a large number of self-assembled monolayer structures. These monolayer structures have been probed using molecular resolution scanning tunneling microscopy. Several of these structures exhibit chirality, and many provide interesting patterns on the nanometer scale. The formation and stability of these structures has been used to probe the interaction energies that govern the self-assembly process for these materials. These detailed structural studies will be discussed.

The chemisorption of alkane phosphonate layers on oxide surfaces also results in the formation of well ordered self-assembled monolayers. The structure and composition of these organic monolayers has been probed using high resolution X-ray photoelectron spectroscopy, particularly employing a novel differential charging technique to distinguish monolayer from multilayer films, and to examine the bonding of the monolayer to the oxide surface.

Many of these organic monolayers exhibit “odd-even” effects in structure. Some exhibit this “odd-even” behavior in reactivity. Examples of these odd even effects will also be discussed.

COLL 384 Catalytic production of fuels from biomass-derived oxygenated hydrocarbons

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Environmental and political problems created by our dependence on fossil fuels, such as global warming and national security, combined with diminishing petroleum resources are causing our society to search for new renewable sources of energy and chemicals. We show how hydrogen can be produced by aqueous-phase reforming of oxygenated hydrocarbons derived from carbohydrates with liquid water at low temperatures (e.g., 500 K). We present the theoretical basis for aqueous-phase reforming, based on density functional theory calculations, and we show experimental results for aqueous-phase reforming at various reaction conditions. We also show how aqueous-phase reforming of sorbitol solutions can be conducted over bi-functional catalysts, containing metal and acidic components, to produce a stream of light alkanes, ranging from C1 to C6. In addition, we show how to produce liquid alkanes ranging from C7 to C15 by combining aqueous-phase reforming reactions with an aldol condensation step to form C-C bonds between such species as 5-hydoxymethylfurfural, furfural, and acetone. Finally, we show how the reforming process can be modified to produce H2:CO gas mixtures from oxygenated hydrocarbons, thereby providing a renewable source of synthesis gas to make fuels and chemicals by well-established catalytic processes developed for the petrochemical industry.

COLL 385 Structure and rheology of amphiphilic block copolypeptide gels

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Amphiphilic block copolypeptides were prepared through transition-metal-mediated polymerization of amino acid *N*-carboxyanhydrides. In aqueous solution these materials form strong hydrogels at low concentrations. The self-assembly process that is responsible for gelation was investigated by measuring the rheological properties of the gels for a variety of molecular architectures: poly-L-lysine-*b*-poly-L-leucine diblock and poly-L-lysine-*b*-poly-L-leucine-*b*-poly-L-lysine triblock copolypeptides.

The self-assembly process is a delicate balance between repulsive and attractive intermolecular forces. The hydrophilic polyelectrolyte segments have stretched coil configurations and stabilize the twisted fibril assemblies by forming a corona around the hydrophobic core. Tuning the molecular architecture and mixing of different block copolypeptides in solution was used to control and optimize hydrogel properties.

Macroscopic rheological data will be presented to elucidate the role of the key intermolecular interactions in the self-assembled structures. For potential applications in tissue scaffolding and drug delivery, molecular architectures were designed which form uniquely stable hydrogels in deionized water as well as various ionic media (salt solutions, buffer solutions, and cell growth media).

Particle tracking microrheology was performed in a microscopic dialysis cell, which enables non-invasive manipulation of the solvent composition in non-crosslinked hydrogel samples. Microrheology provided a much more complete picture of the microscopic structure, revealing the occurrence of reversible microscopic phase separation upon the addition of salt. Data will be presented on the structure and dynamics of these morphological changes.

COLL 386 The interaction of DNA and other amphiphilic polyelectrolytes with ionic surfactants: Bulk vs. interfaces

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The interaction between polyions and oppositely charged amphiphilic ions involves a combination of hydrophobic and electrostatic forces. On the basis of a review of polymer-surfactant association in bulk, the behavior of these mixed systems on solid surfaces is discussed. In particular, we consider the adsorption of mixtures of polyelectrolytes and oppositely charged surfactants on polar and nonpolar surfaces. It is found that, depending on concentration, an ionic surfactant can either induce additional polyion adsorption or induce desorption. Kinetic control of adsorption and, in particular, desorption is typical. Important consequences of this include increased adsorption on rinsing and path dependent adsorbed layers.

DNA is a polyelectrolyte with hydrophobic groups; the latter induce self-assembly and affect adsorption and the association with surfactants and other amphiphilic polymers. Polyvalent cationic cosolutes induce DNA complexation, compaction and protection. DNA adsorbs on a hydrophobic surface with a low adsorbed amount and with an extended conformation. On addition of a cationic surfactant, the adsorbed amount increases strongly at the same time as DNA compacts. As the surfactant is removed, DNA decompaction may occur. On a hydrophilic anionic surface DNA does not adsorb but adsorption can be induced by a cationic surfactant. Various aspects of the interfacial behaviour of mixed DNA-surfactant systems are presented. These include the study of adsorption on hydrophobic and hydrophilic surfaces by ellipsometry, and the forces between DNA-covered surfaces by surface force apparatus. Different surfactant types are studied including the combination of cationic and anionic surfactant. Both thermodynamic and kinetic aspects are included. Kinetics play a crucial role as shown by an effectively irreversible DNA adsorption.

COLL 387 Micellisation of block and graft copolymers of n-butyl acrylate and acrylic acid

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Block and graft copolymers, poly(n-butyl acrylate)-block/graft-poly(acrylic acid), have been synthesized via Atom Transfer Radical Polymerization of n-butyl acrylate and tert-butyl acrylate, followed by hydrolysis of the tert-butyl ester groups. The cmc of the copolymers in water was determined by fluorometry of pyrene and by fluorescence correlation spectroscopy. The structure of the micelles, as determined by static and dynamic light scattering, small-angle neutron scattering and cryo-transmission electron microscopy, strongly depends on the polymer structure and morphology as well as on pH and salinity. The micelles have a frozen core, which becomes dynamic after partial (10-20%) hydrolysis of the n-butyl groups.

COLL 388 Novel smart amphiphilic polymer conetworks and gels

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Two new types of smart (intelligent, responsive) nanostructured amphiphilic polymer conetworks and gels have been synthesized and investigated by us. One of them is a series of pH-responsive conetworks composed of covalently bonded extremely hydrophobic polyisobutylene (PIB) and poly(methacrylic acid) (PMAA) polyelectrolyte. Controlled pH response was found for these conetworks as a function of composition. The other class of intelligent conetworks was made of poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) and PIB exhibiting rapid temperature responsive behavior upon changing the temperature in the range of the lower critical solution temperature (LCST) of PDMAEMA. The response intensity shows a unique, unexpected dependence on composition. These new materials exhibit significantly better physical properties (strength in particular) than those of corresponding hydrogels, and this makes them suitable for many potential applications.

COLL 389 Amphiphilic homopolymers for interaction with proteins

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Abstract: The interaction of proteins with polyelectrolytes is an exciting area of research and has been studied extensively in the last few years. However, most of the studies have focused only on the structural component of protein-polyelectrolyte complex and functional task of the above complex is not explored well. Also, work in this area predominantly involves, the use of commercially available polyelectrolytes and there are very few reports based on custom-designed amphiphilic polyelectrolytes. To this end, here, we show the interaction of cationic protein with custom-designed anionic amphiphilic homopolymers. The binding of polymer to target protein results in complete loss of enzymatic activity against certain substrates. Nature of the polymer-protein interactions that leads up to this substrate selectivity will be discussed

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COLL 390 Behaviors of cationic surfactants in oppositely charged polyelectrolyte brushes formed by physiosorption of amphiphilic diblock copolymer

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We have investigated effects of cationic surfactant (cetyl trimethyl ammonium bromide, CTAB) on sodium poly(styrene sulfonate) brushes in the presence of 1 mM NaNO3 by a use of ellipsometry and a surface force apparatus (SFA). Brushes were formed by physisorption of amphiphilic diblock copolymer, poly(t-butylstyrene)-b-sodium poly(styrene sulfonate) (NaPSS). There are three regimes in the adsorption process of CTAB to brushes involving an electrostatic interaction between surfactant/brushes and hydrophobic interaction between surfactants. As the concentration of CTAB increased in the bulk solution, it was adsorbed reversibly exchanging with counter ions of brushes in the beginning. Then, surfactants along brushes began to interact each other hydrophobically reinforcing the binding between brushes and surfactants as a whole. This caused the adsorption irreversible. With further CTAB added into the bulk solution, micelles were formed in brushes that had excess positive charges on the surfaces.

COLL 391 Self-association of amphiphilic statistical copolymers in aqueous media

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Amphiphilic statistical copolymer samples of sodium 2-(acrylamido)-2-methylpropanesulfonate (NaAMPS) and n-hexyl methacrylate (C6MA) with different degrees of polymerization and compositions were prepared by reversible addition-fragmentation chain transfer copolymerization, and their self-association in 0.1 M aqueous NaCl was studied by light scattering, fluorescence, viscometry, and size exclusion chromatography. Major components of the copolymer samples were aggregates consisting of 2-7 polymer chains and possessing 1-5 hydrophobic microdomains, and their structures were analyzed in terms of the uni-core or multi-core micelle model. The structure of the aggregates was strongly dependent on the degree of polymerization of the copolymer. Similar studies were made also for statistical copolymer samples of N-acryloyl-amino acids (sodium salt) and N-dodecylmethacrylamide, and the results were compared with those for the NaAMPS/C6MA copolymer.

COLL 392 Investigation of the effects of polyelectrolyte structure and electrolyte addition order on the mechanism of complex coacervate formation

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Complex coacervates, which are used in a variety of applications, are formed as a result of the interactions of two macromolecules, or a macromolecule and an association colloid, of opposite charge. High-throughput screening formulation methods were used to construct multi-component phase diagrams covering a wide range of polymer and surfactant concentrations. Using cationic poly(vinyl pyridines) and polysaccharides with anionic surfactants we have explored the impact of polymer structure, charge accessibility, and electrolyte addition order on the degree of coacervation. We found that increasing charge density and/or molecular weight caused an increase in coacervation. However, an increase in the accessibility of the cationically charged moiety significantly increases the compositional range of coacervation, independent of molecular weight. In the addition order studies, we see a probable collapse of the polyelectrolyte structure with the addition of electrolyte prior to surfactant addition, which leads to a wide variation in the compositional range of coacervation.

COLL 393 Interfacial properties of aqueous surfactant mixtures: A Monte Carlo study

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Although experiments are often carried out for single-surfactant systems, most technological applications rely on surfactant mixtures. Configurational-bias Monte Carlo simulations are used here to investigate the interfacial enrichment, structure, and hydrogen-bonding at the liquid/vapor interface for solutions of water + 1-butanol + 2-ethoxyethan-1-ol. The TraPPE and TIP4P force fields are used for the surfactants and water, respectively. The 1-butanol molecules are mostly found in the outermost layer with their alkyl tails pointing preferentially toward the vapor phase, i.e. their long axis is aligned perpendicular to the surface. In contrast, many of the 2-ethoxyethan-1-ol molecules are found in a subsurface layer, i.e. sandwiched between the 1-butanol layer and the bulk aqueous phase. The great excess of hydrogen bond acceptor sites allows the 2-ethoxyethan-1-ol to form this bridging layer, and molecules in this layer are preferentially found with their backbone parallel to the surface. As the overall concentration of 2-ethoxyethan-1-ol is increased, its concentration in the bulk region of the aqueous phase increases and, more importantly, the water content in the organic phase increases dramatically. Similar to the aqueous phase, the outer surface of the organic phase is mainly occupied by 1-butanol molecules with 2-ethoxyethan-1-ol molecules populating the subsurface layer.

COLL 394 Molecular modeling of transport across surfactant-covered interfaces of microemulsions

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The process of mass transfer across surfactant-covered interfaces of microemulsions plays a key role in a wide variety of applications such as separations, reactions, and drug delivery. The densely packed surfactant monolayer offers a significant resistance to the mass transfer. We present results of molecular modeling of solute transport across an interface of hexadecane-in-water microemulsions covered by Brij surfactants. The studies are performed using a coarse-grained molecular dynamics model. This model is validated by comparison of equilibrium microemulsion properties with experimental data. We develop an effective stochastic model for the solute transport across the interface. The components of this model (the mean potential force and the solute diffusivity) are obtained using the constrained molecular dynamics simulations. In order to gain detailed understanding of the mechanism of the solute transport, we analyze internal microstructure of the surfactant monolayer and correlations between dynamics of the solute and dynamics of the surfactants.

COLL 395 Continuum formulation of the Scheutjens-Fleer lattice statistical theory for homopolymer adsorption from solution

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Homopolymer adsorption from a dilute solution on an interacting (attractive) surface under static equilibrium conditions is studied in the framework of a two-fluid Hamiltonian model which makes use of the density of chain ends n_e and utilizes the concept of the propagator G describing conformational probabilities to locally define the polymer segment density or volume fraction phi; both n_e and phi enter into the expression for the system free energy. The propagator G obeys the Edwards diffusion equation for walks in a self-consistent potential field. The equilibrium distribution of chain ends and, consequently, of chain conformational probabilities is found by minimizing the system free energy. This results in a set of model equations that constitute the exact continuum-space analogue of the Scheutjens-Fleer (SF) lattice statistical theory for the adsorption of interacting chains. Since for distances too close to the surface the continuum formulation breaks down, the continuum model is here employed to describe the probability of chain configurations only for distances z greater than 2l, where l denotes the segment length, from the surface; instead, for distances z less than or equal 2l, the SF lattice model is utilized. Through this novel formulation, the lattice solution at z=2l provides the boundary condition (b.c.) for the continuum model. The resulting hybrid [lattice for distances z less than or equal to 2l, continuum for distances z greater than 2l] model is solved numerically through an efficient implementation of the pseudo-spectral collocation method. Representative results obtained with the new model and a direct application of the SF lattice model are extensively compared with each other and, in all cases studied, are found to be practically identical.

COLL 396 Lattice Monte Carlo simulations of confinement effects on lyotropic surfactant liquid crystals

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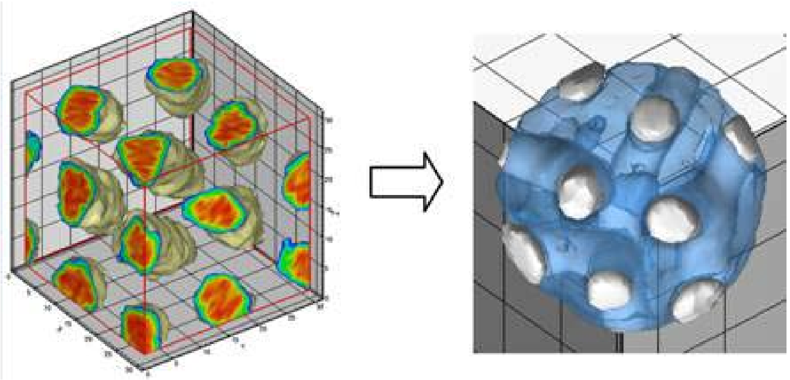
Novel nanostructured materials have recently been synthesized using lyotropic liquid crystals confined in slabs (thin films), cylinders (anodized alumina pores), and spheres (droplets). We report coarse grained mesophases simulations aimed at understanding how confinement in these geometries affects the mesophases type and orientation, and the occurrence of defects. 2D hexagonal close packed (HCP) cylindrical phases align parallel to preferential (hydrophilic/hydrophobic) flat walls, and the number of micelle layers is discretized. In cylindrical and spherical preferential cavities, the number of layers is also discretized, but HCP cylinders are lost

in favor of perforated layers, rings, or helices. In contrast, chemically neutral (CN) surfaces favor hemimicelles or orthogonally oriented cylinders. In CN slabs and cylinders, HCP micelles span the width of the cavity. In spheres, the micelles orient radially at the surface and are randomly interconnected in the interior. We compare the simulation results with expectations from simple geometric and energetic considerations.



COLL 397 Nanoparticle-surfactant composite self-assembly and surface patterning

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By using Coarse-grain (CG) methodology we have studied the nanoparticel-copolymer composites self-assembly and adsorption onto solid surfaces. Simulations demonstrated the possible highly patterned surface formation using the nanoparticle-copolymer composites. The present simulations reproduced experimental observations such as micelle incorporated Quantum dot formation and pattern formation during surfactant adsorption onto solid surfaces.In addition to complimenting the existing theoretical predictions and experimental observations, present simulations provide insights into nanoparticle-copolymer self-assembly mechanism. The N-C composites adsorption onto solid surfaces provide intutive directions for the further experimental strategies for the well controlled patterned surfaces.

COLL 398 Role of temperature on electro-viscous flow in a rectangular batch cell

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Electro-viscous types of flow are studied under non-isothermal conditions to assess the influence of thermal change on electroosmotic velocity profiles. This subject is a key factor on the study of electrokinetic processes, such as electro-assisted drug delivery, micro-electrophoretic separations, soil remediation, and material processing just to name a few. In a recent work, Arce and Oyanader* proposed a novel and simpler solution of the complete Poisson-Boltzmann equation for systems where the electrostatic potential is not affected by non isothermal conditions. On this contribution, the analysis of the previous contribution of Arce and Oyanader has been extended to those cases where temperature profiles develop across a rectangular batch cell and cannot be neglected in the prediction of electrostatic potentials. In particular, the application of values of electrical field that will promote a temperature gradient inside the system leads to a situation where the electroosmosis alone may promote distinct flow regimes.

(*) Oyanader, M., Arce, P., "A New and Simpler Approach for the Solution of the Electrostatic Potential Differential Equation. Enhanced Solution for Planar, Cylindrical and Annular Geometries," Journal of Colloid and Interface Science, 2005, 284, 315.

COLL 399 How cells respond to molecular positioning of signal molecules and transmembrane receptors

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In order to study the response of cells to the molecular arrangement of single integrins in cell adhesion, we designed a hexagonally close-packed rigid template of cell adhesive gold nano-dots coated with cyclic RGDfK peptide via diblock copolymer self-assembly. The diameter of the adhesive dots is < 8nm allowing the binding of one integrin per dot. These dots are positioned with high precision at 28, 58, 73 and 85nm spacings. A distance of ≥ 73nm between the dots hampers cell attachment and spreading, thereby dramatically reducing the formation of focal adhesion and actin stress fibers. We attribute these cellular responses to restricted integrin clustering rather than an insufficient number of ligand molecules in the cell-matrix interface since "micro-nanopatterned" substrates consisting of alternating fields with dense and no nano-dots support cell adhesion. We propose that the range between 58 - 73nm is a universal length scale for integrin clustering and activation.

COLL 400 Electrochemically programmable bioactive interfaces at ß-cyclodextrin SAMs

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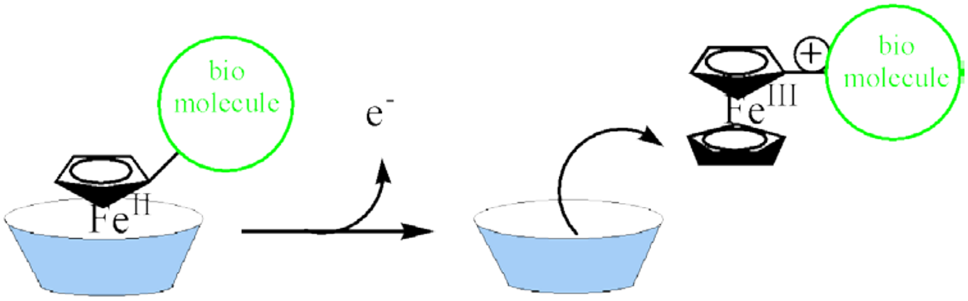
Self assembled monolayers (SAMs) of cyclodextrin can be used as a template for the reversible electrochemical patterning of substrates. This work describes electrochemical means of controlling the formation of complexes between a variety of host molecule SAMs (comprised of derivatives of ß-cyclodextrin) and analyte guest molecules based on ferrocene. We have succeeded in linking biotin to ferrocene via an ethylene glycol bridge and demonstrating that the species is active towards the adsorption of streptavidin. With such programmable streptavidin surfaces we can create patterns with a wide range of biotinylated biological species. A combination of electrochemical techniques, atomic force microscopy, and quartz crystal microbalance measurements show that binding functionality can be controlled, maintained, and monitored in aqueous electrolytes over a practical range of potentials for sensing. Use of such switchable films for the creation of programmable patterns of antibodies is described.



COLL 401 Selective adsorption of polymer- and nucleic base-functionalized colloids

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The selective adsorption behavior of polymers and colloidal particles is of great interest for the production of nano and micro-scale features within organic thin films. We have previously demonstrated the in-situ patterning of polyelectrolyte adsorption by chemical templating of surfaces. Now, we extend this approach to colloidal particles by functionalizing them with a polymer capable of directing adsorption, allowing for the selective self-assembly of multi-component colloidal arrays. Unlike side-by-side patterns of multilayer films, these colloidal assemblies can be easily and faithfully transferred from the original surface template directing their assembly to a new matrix better suited to the final application. In order to design more complex arrays, we have increased the range of interactions used to guide adsorption and sought out species with specific recognition abilities. Multiple hydrogen bonding, being both highly specific and highly tunable via temperature and pH, is ideally suited to this purpose and so we first explored the application of nucleotide base pairing to selective adsorption. RNA homopolymers were used both for functionalization of polystyrene latex colloids and for chemical patterning of surfaces; we have also synthesized base-terminated silanes for more robust functionalization of silicon surfaces and colloids. We have also studied the self-assembly in solution of microspheres dually functionalized with complementary nucleic bases.

COLL 402 Enhanced cell adhesion and confinement on gradient nanotopography

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We report the design and use of a self-assembled chemical gradient on gold films having a nanostructured topography to control the attachment, adhesion and two-dimensional confinement of mammalian cells. By using self-assembled monolayers (SAMs), we created patches of cell adhesion areas in µm-size squares along the gradient steepness surrounded by a bio-inert chemistry that resists protein adsorption and cell adhesion. When cultured on this gradient nanotopography, mammalian cells attach and reach confluency within the squares more rapidly on the high topography than at the low topography. However, after cells grow confluent on all squares on the gradient nanotopography, cells are confined longer on high topography than low topography. Both of these two results suggest advancements for doing cell biology and cell-based biotechnology by using carefully crafted nanotopography. We will present a proposed mechanism and supporting results on how the nanotopography enhances the adhesion and confinement of mammalian cells.

COLL 403 Guiding cell migration by microarray amplification of natural directional persistence

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Directional control of cell migration is essential for engineering tissues with defined cellular architectures, promoting wound healing, and non-invasively manipulating cells in vitro. Directional migration of cells can be induced by gradients of chemoattractants (chemotaxis) and cell-substratum adhesion strength (haptotaxis). However, because directional control is set by the steepness of the gradients, cell migration can be directed only over limited distances on simple, typically linear, paths. Here we report a new approach, Microarray Amplification of Natural Directional Persistence (MANDIP), to guide the long-range directional migration of attached mammalian cells. Amplification of directional persistence occurs through the asymmetric positioning of microarray islands and restriction of lamellipodia attachment, and thus migration, to one preset direction. Like one-way signs, these microarrays impose directionality with overwhelming compliance and simultaneously guide the migration of arbitrary number of cells independently over arbitrary paths without chemoattractants, external fields, or mechanical manipulation. This ability to control the directional migration of large number of cells opens up new avenues for non-invasive manipulation, transport, and delivery of cells.

COLL 404 Bionanofabrication with polymers and enzymes

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I will present recent examples of work from a collaboration between my laboratory and Stefan Zauscher's on the situ fabrication of nano-microscale polymer structures that can modulate biological events at artificial surfaces. The fabrication of stimulus-responsive nanoscale arrays of a genetically engineered polypeptide by DPN that enables a few hundred-protein molecules to be captured from solution, displayed in a functionally active conformation at the surface, and then reversibly desorbed from the surface will be described. In the second example, the in situ synthesis of nanometer thick brushes of an oligoethyleneglycol-functionalized polymer by surface-initiated polymerization will be described, and the extension of this methodology to the microscale by soft lithography and to the nanoscale by DPN. These nanometer thick polymer brushes show extraordinary resistance to protein adsorption and the adhesion of cells and provide a powerful platform to examine the interaction of cells with biochemical and topographical cues at length scales ranging from the nano-microscale. In more recent work, I will summarize recent results of nanoscale enzymatic manipulation of DNA, in which we have harnessed the catalytic power of enzymes at the surface at nanoscale dimensions. I will show how terminal deoxynucleotidyl transferase, which repetitively adds mononucleotides to the 3' end of a short DNA initiator, can be used to rapidly fabricate DNA nanostructures up to 120 nm high with lateral dimensions from 0.1 to 4 mm. These DNA nanostructures can direct the step-wise formation of composite molecular ensembles consisting of natural or unnatural nucleotides and serve as a structural component for more complicated two- or three-dimensional nanostructures by selectively docking other molecules along the z-direction with nanometer-level precision.

COLL 405 DNA strands as Gutenberg movable type: Supramolecular NanoStamping

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The recent interest in nano-science has catalyzed research in the development of nano-fabrication techniques. New highly versatile nanolithography techniques based on scanning probe microscopes have been reported. A wide variety of organic and inorganic substrates can be patterned either by inducing localized chemical modifications of or by forming self-assembled monolayers (SAMs). Unfortunately, they all have in common the same drawback: they are extremely slow. A new versatile method (Supramolecular NanoStamping, SuNS) that will allow for the stamping of nanofabricated substrates will be presented. Patterns generated by many nanofabrication techniques can be used as stamps. This method is based on a four-step approach: 1) A patterned SAM of single-strand-DNA terminated molecules is formed. 2) Complement DNA strands are assembled on the patterned DNA SAMs. The complement DNA is functionalized on one end (the one that is far from the substrate) with a chemical moiety able to react with a surface (e.g. thiol/gold or siloxane/glass). 3) A second substrate is brought close to the first, allowing for the formation of chemical bonds between the reactive groups on the complement DNA and the substrate surface. 4) The DNA double helices are dehybridized by mild heating. The two substrates are then separated. After this process the first substrate is left in its initial state and the second is a replica of the first one, as needed for a stamping technique. One of the main advantages of this method is that multiple DNA strands (each encoding different information) can be printed at the same time, thus allowing for a complex chemical pattern to be formed, much like Gutenberg movable type. The parallel printing of a pattern formed by two DNA strands will be presented.

COLL 406 Binding and patterning of organic molecules on silicon surfaces

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Attaching functional organic layers to silicon surfaces is emerging as one of the promising approaches in the development of new semiconductor-based microelectronic devices and biosensors. It provides opportunities for incorporating molecular recognition, chirality, chemical/biological sensing, light emission/detection and lubrication for various technological needs. Recent systematic investigations on chemical reactions of organic molecules on silicon surfaces clearly demonstrated that both Si(100) and Si(111)-7x7 can act as reagent-like substrates with a high reactivity for covalent binding of different classes of organic functionalities. Reaction mechanisms including [2+2]-cycloaddition, [4+2]-cycloaddition, and dative-bonding addition have been revealed and will be discussed, providing a molecule-level understanding on reaction mechanisms, chemical and surface-site selectivities at organic/silicon hybrid interfaces. In addition, new approaches for fabricating organic nanopatterns using self-assembled templates on silicon surfaces will be introduced, which can be useful in growing organic nanomaterials for developing nano- or molecular-scale devices.

COLL 407 Photochemical functionalization of diamond surfaces: Mechanism and properties

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Diamond is a material with many remarkable properties, including outstanding chemical and electrochemical stability. Functionalization of diamond surfaces with molecular systems can infer desirable properties including recognition of specific biomolecules, resistance to nonspecific adsorption of proteins, and electrical properties of interest for electronic sensing. Surprisingly, the functionalization occurs by illumination at 254 nm, where the diamond bulk and the molecules of interest are almost completely transparent. Using a variety of vacuum – based and solution-phase measurements, we have recently elucidated the mechanism of functionalization. These results shown that it is initiated by direct ejection of electrons from the diamond surface; on diamond this can occur with sub-bandgap illumination due to diamond's unusual property of negative electron affinity. In this talk I will review recent work on diamond functionalization and the prospects for generalizing this "electon-ejection" chemistry as a method for functionalizing surfaces of other materials.

COLL 408 Surface organometallic chemistry: From surface functionality to functional surfaces

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Indium tin oxide (ITO) is a ubiquitous anode material for use in optoelectronic devices, and considerable effort has gone into developing and testing models aimed at enhancing hole injection from ITO into an organic overlayer. Among these models is an elegant one based on simple concepts of electrostatics: organization of a dipole layer at the surface of an ITO electrode is predicted to affect its work function and, hence, the hole injection barrier. Surface organometallic chemistry was used to introduce such dipoles, and systematic modification of structures of surface-bound complexes was shown to affect the ITO work function, also systematically. Current densities in simple hole-only devices also correlated with these surface dipoles. In this way, a bright and efficient OLED was prepared through appropriate choice of surface complex ligation.

COLL 409 Fluorescence labeling of surface species (FLOSS) as a probe of chemical composition of complex interfaces

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Determining the chemical composition of heterogeneous two-dimensional systems remains challenging. For example, how does one detect a low concentration of alcohol (-OH) functionality in a sea of carboxylic acid (-COOH) groups? Covalent fluorescent labeling of surface species (FLOSS) allows the inherent sensitivity of fluorescence spectroscopy to be exploited to identify and quantify the concentrations of functional groups on surfaces. FLOSS enables the identification of intermediates in the UV photoreactivity of octadecylsiloxane (ODS) self-assembled monolayers (SAMs), and the nature of oxygen containing functionality on carbon nanotubes.

COLL 410 The formation of organic monolayers on alloy oxide surfaces

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Nickel containing alloys are important biomaterials used in arterial stabilization implants. This presentation outlines initial steps in the process of controlling the surface properties of the implant material by the organofunctionalization of the native oxide surface with monolayers of alkylorganic acids. Control of the surface properties will allow us to ease complications caused by non-specific adsorption fibrous tissues, cells, and platelets to the surface. Implant materials, stainless steel 316L and nitinol, are studied. The effect of head group acidity, chain length, tail group functionality, and surface roughness is analyzed. By varying reaction conditions, organic acids of various chain lengths can be successfully used to form monolayers on the native oxide surface of SS316L and nitinol. Further, the tail groups are presented in an accessible and reactive position so that the surface can be further modified through reactions at the surface.

COLL 411 Si(114)-(2x1): A nano chem kit for comparative molecular surface functionalization

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Si(114)-(2×1) is a stable high-index surface oriented 19.5° between (001) and (111). The equilibrium surface reconstruction is comprised of parallel rows of dimers, rebonded atoms, and tetramers, with all the rows oriented along the same crystallographic direction. The different Si(114) structural motifs within each row have distinct electronic structures, making this surface an ideal template for studying the relationship between adsorption site geometry (including symmetry), local electronic structure, and chemisorption of organic molecules on clean silicon surfaces. In this work, transmission Fourier transform infrared (FTIR) spectroscopy, scanning tunneling microscopy (STM) and density-functional-theory (DFT) calculations are used to determine the basic chemical structure and orientation of ethylene chemisorbed on Si(114)-(2×1). The FTIR spectra are consistent with di-sigma bonding of ethylene. A detailed analysis of the strong angular and polarization dependence of the C-H stretching mode intensities indicates ethylene chemisorbs with the C-C bond axis parallel to the structural rows oriented along the [-110] surface direction. Using atomic-resolution STM, we identified three common adsorption structures located at the dimer, rebonded atom, and tetramer sites. In correlation with the FTIR and DFT results, these structures can be identified as [2+2] cycloaddition products, bridged rebonded atoms, and [4+2] cycloaddition products, respectively. The order of surface site reactivity is found to be rebonded atoms > dimers > tetramers. Reasons for this reactivity trend will be discussed.

COLL 412 Assembly and functionalization of olefin-terminated monolayers on Si(111) with the Grubbs' catalyst

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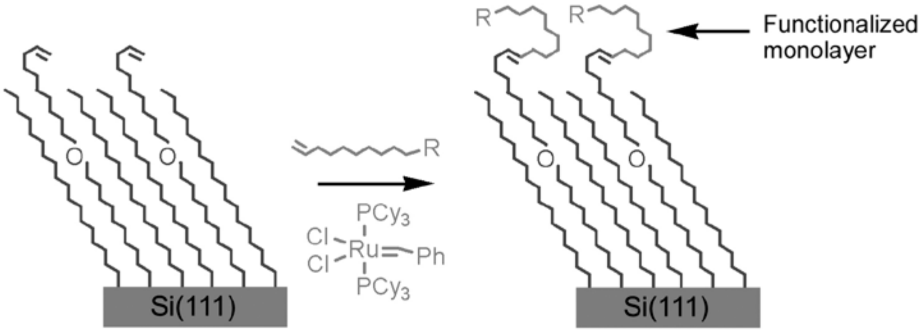
We recently developed a mild method to assemble mixed monolayers of $CH_2=CH(CH_2)_9O(CH_2)_9CH=CH_2$ and 1-octadecene on hydrogen-terminated Si(111) using 0.1 mole % of 2,2,6,6-tetramethyl-1-piperidinyloxy. We characterized these monolayers by contact angle goniometry, horizontal attenuated total reflection infrared spectroscopy, and x-ray photoelectron spectroscopy. These monolayers were terminated with olefins that were further reacted with the Grubbs' catalyst. The surface was functionalized by cross metathesis with olefins in solution. Four different olefins were used to functionalize the surfaces with alcohols, aldehydes, carboxylic acids, or alkyl bromides. We determined the optimal ratio of $CH_2=CH(CH_2)_9O(CH_2)_9CH=CH_2$ to 1-octadecene on the monolayer to yield surfaces exposing the highest concentration of cross metathesized product. These surfaces were patterned with microfluidics by reacting the Grubb's catalyst with the monolayer and then flowing 5-norbornene-2-carboxylic acid through the channels. Patterned monolayers were characterized by scanning electron microscopy.



COLL 413 Fluorescence and rheological study of a fluorescently labeled associative polymer

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The hydrophobe of a series of Hydrophobically modified Alkali Swellable Emulsion polymers (HASEs) was replaced by the chromophore pyrene. Because the fluorescence of pyrene changes whether it is present as an individual unit or as an aggregate, fluorescence can be used to monitor the behaviour of the various pyrene species present in solution. After demonstrating that using pyrene as a hydrophobe does not affect the overall viscoelastic properties of the HASE solutions, a study of the interactions of the pyrene-labelled HASE with the surfactant sodium dodecyl sulphate was conducted. The fraction of aggregated pyrenes was determined quantitatively and was found to decrease substantially as the surfactant is added to the HASE solution. Of particular interest is the correlation that exists between the number of pyrenes per mixed micelles and the viscosity of the solution. It will be discussed in this presentation.

COLL 414 Mesoglobules of hydrophobically-modified telechelic poly(N-isopropylacrylamides) in water probed by light scattering, fluorescence spectroscopy, and microcalorimetry

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Telechelic hydrophobically-modified poly(N-isopropylacrylamides) (HM-PNIPAM) with n-octadecyl termini were obtained by RAFT polymerization of NIPAM in dioxane in the presence of S-1-n-octadecyl-S'-(&alpha,&alpha'-dimethyl-&alpha''-N-n-octadecylacetamide)trithio-carbonate as a chain transfer agent. Their molar mass (Mn) ranged from 12,000 to 49,000 g mol-1 with a polydispersity index lower than 1.20. In cold aqueous solution these polymers form flower micelles that collapse into dense mesoglobules above the phase transition temperature. We examined the influence of polymer chain length, temperature, and the presence of electrolytes on the stability and eventual aggregation of collapsed globules. We have employed dynamic and static light scattering measurements to gain information on the size and aggregation number of the micelles. Static fluorescence and fluorescence polarization measurements were carried out to determine the critical micelle concentration of telechelic PNIPAMs and to assess the microviscosity of the core of hydrated micelles and of collapsed globules. The results are discussed in the context of the current understanding of the stability of mesoglobules of thermoresponsive polymers in dilute aqueous solutions above their cloud point.

COLL 415 The effect of polydispersity on the self-assembly of PEO-PDEAMA block copolymers in dilute solution

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Block copolymers consist of two or more chemically homogeneous polymer fragments joined together by covalent bonds to form more complex macromolecules. A series of amphiphilic poly(ethylene oxide)-block-poly(N,N-diethylaminoethylmethacrylate) block copolymers have been synthesised by ATRP using PEO-based macroinitiators. Both the PEO and methacrylate block lengths have been varied systematically. By varying the reaction conditions, the polydispersity (PDI) of the methacrylate block has been varied between 1.3 and 2. These diblock copolymers dissolve molecularly at low pH, but self-assemble at high pH where the methacrylate blocks are deprotonated and hence hydrophobic. Depending on the relative block lengths, micelles, worm-like micelles or vesicles can be prepared. Here, we show that even relatively high polydispersity (PDI >1.9) in the hydrophobic block does not preclude efficient self-assembly. We also discuss the effect of salt on the self-assembly of these amphiphilic block copolymers.

COLL 416 Impact of 2-D dilational viscoelasticity of adsorption layers of hydrophobically modified chitosans on the stability of emulsions

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Hydrophobic modification of polyelectrolytes (PE) either by covalent alkylation or by electrostatic complex formation with oppositely charged surfactants in the mixed solutions increases considerably the surface activity of PE. At the same time, the hydrophobic interactions in the adsorption layers of alkylated polyelectrolytes (polysoaps) and surfactant-polyelectrolyte complexes (SPEC) lead to the formation of the gel-like interfacial films with anomalously high viscoelastic properties. The dilatational rheological properties of adsorption monolayers of cationic polysoaps on the basis of chitosan, on the one hand, and SPECs formed between chitosan and alkylsulphates, on the other hand, at the air-water interface have been studied by the axisymmetric bubble shape analysis. The kinetics of adsorption of hydrophobically modified chitosans and the viscoelastic properties of their adsorption layers produce a remarkable impact on the aggregative stability of emulsions

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COLL 417 Self-assembly of polystyrene-block-poly(2-vinylpyridine)-block-poly(ethylene oxide) in aqueous media

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Polystyrene-block-poly(2-vinylpyridine)-block-poly(ethylene oxide) copolymers, PS-PVP-PEO, form micelles in both acidic and basic aqueous media. In acidic media, the partially protonized poly(2-vinypyridine) is water-soluble, while in neutral and basic media, the deprotonized PVP collapses and forms a compact middle layer around the PS core. By a stepwise dialysis in ternary 1,4-dioxane - methanol - acidic water mixtures, it is possible to prepare very small monodisperse micelles formed by less than 10 copolymer chains. In this case, the small PS cores are soft (not glassy). Even though the unimer exchange between micelles is kinetically frozen, the PS chains in cores may reorganize and micelles show a high tendency to form micellar clustes. The clustration, which is reversible in the low pH region, was studied by a combination of light scattering and fluorescence techniques, AFM, etc. The time-resolved solvent relaxation study with probes incorporated in micellar shells revealed important changes in the solvation of PEO with pH.

COLL 418 Solution properties of hydrophobically modified phosphorylcholine-based polymers synthesized via RAFT polymerization

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Hydrophobically-modified block copolymers consisting of N-isopropylacrylamide [NIPAM] units, phosphorylcholine (PC)-based units and an octadecyl end group were prepared by Reversible Addition-Fragmentation chain Transfer copolymerization (RAFT), which allowed precise control of the polydispersity and block length, and permitted specific attachment of one end group. Studies by dynamic light scattering (DLS) and 1H NMR spectroscopy indicate that in water kept below the cloud point temperature of PNIPAM the copolymers form micelles via association of the hydrophobic tails, whereas in chloroform they form reverse-micelles via ion-pair driven association of the phosphorylcholine groups. The critical aggregation concentration (cac) of the copolymers in water was determined by isothermal titration calorimetry (ITC) as a function of temperature. The interactions of the copolymers with hydrophilic and hydrophobic surfaces were investigated by surface plasmon resonance (SPR) and quartz crystal microbalance (QCM).

COLL 419 Spontaneously forming hydrogel from amphiphilic random- and block-type phospholipid polymers

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Mixing of aqueous solutions of two water-soluble phospholipid polymers, such as poly[2-methacryloyloxyethyl phosphorylcholine(MPC)-co-n-butyl methacrylate] and poly(MPC-co-methacrylic acid) spontaneously forms a hydrogel without any chemical treatments due to hydrogen bonding formation between the carboxyl groups. A random and an ABA-block-type MPC copolymer having carboxylic acids have been designed to enhance this property. The Raman spectroscopic analysis and the theological study of the dissolution behaviors indicated that the gel formation occurred due to inter- and intra-molecular hydrogen bonding formation between the carboxyl groups in the random polymer. Since the block-polymer chains aggregate in the aqueous medium and transform into a hydrogel network structure, it needed much more gelation time than the random-polymer. We concluded that the properties of these MPC polymer hydrogels could be controlled by

not only the chemical structure of the polymer but also the monomer unit sequence containing carboxyl groups.

COLL 420 Two-dimensional self-assembly of poly(ethylene oxide)-*b*-poly(ε-caprolactone) copolymers

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Monolayers of linear and star-shaped amphiphilic Poly(ethylene oxide)-*b*-Poly(ε-caprolactone) copolymers (PEO-*b*-PCL) were studied at the air-water interface by surface pressure-mean molecular area (π-MMA) isotherms and compression-expansion hysteresis experiments**.** The π-MMA isotherms of the linear copolymers exhibited three phase transitions at 6, 11 and 14mN/m, whereas only one transition at 14mN/m was observed for the star-shaped copolymers. The transition at 14mN/m arises from crystallization of the PCL segments and the transitions at 6 and 11mN/m are thought to arise from PEO dissolution in the aqueous subphase. The absence of the two PEO phase transitions for the star-shaped copolymers indicates a negligible surface activity of the star-shaped PEO core compared to the linear PEO analogue. Atomic Force Microscopy imaging of the Langmuir-Blodgett films showed the presence of crystalline domains independent of the surface pressure, indicating that the Langmuir monolayers undergo morphological changes (additional crystallization) during transfer to less hydrated solid surfaces.

COLL 421 Biology as a starting point for tribological interface design

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Nature has constructed a number of exquisite lubrication systems, ranging from the synovial joints in our hips to the slimy trail of the snail on our driveways. All of these are based on water and most involve lubricant additives that lead to the formation of brush-like structures on the sliding surfaces. In many cases, at least one of the contacting surfaces is soft. All this is in contrast to most man-made lubricated machinery, where the lubricant is oil and the surfaces are hard. We have attempted to imitate nature by grafting brush-like polymeric structures onto a number of hard and soft surfaces, and we have investigated the mechanisms by which these systems reduce friction in an aqueous environment, both on the nano- and macro-scales. The results are of interest, not only as model systems to better understand natural lubrication mechanisms, but also as lubrication approaches with potential industrial applications.

COLL 422 Chemical origins of sensory perception: Nanotribology of keratin cosmetic substrates

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Sensory perception of hair and skin, especially smoothness and texture, are macroscopic evaluations often difficult to explain from a microscopic level. In addition, the cosmetic support (hair and skin) can be considered as bio-nanocomposites of extreme complexity. Thanks to the advances in Scanning Probe Techniques and Electron Microscopy, our studies in bio-nanotribology have been able to help explain the chemical foundations of friction on these biological substrates. We will present a review of past and on-going studies in our laboratory that include among others, the effect of naturally-grafted fatty acid monolayers on hair, the nanomechanics of skin constituents, corneocytes, the infuence of external parameters (i.e. humidity, light exposure, etc.).

COLL 423 Biotribology: Lubrication and wear of articular cartilage

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Studies aimed at exploring possible connections between tribology and mechanisms of synovial joint lubrication and degeneration (e.g., osteoarthritis) have been carried out using bovine and human cartilage and techniques designed for "in vitro" measurements of cartilage wear and friction under controlled conditions. The results clearly demonstrate the importance of biochemistry of the fluid as well as of the cartilage on wear and damage under reciprocating sliding contact conditions. For example, certain constituents isolated from bovine synovial fluid by Swann significantly reduce cartilage wear when added to a buffered saline solution. Furthermore, pretreatment of cartilage with collagenase-3, an enzyme found in osteoarthritic joints, increased wear by almost 3-fold. In a recent collaborative study of the wear-resistance of repaired articular cartilage, 16 specimens from the knee joints of eight Swedish patients were examined in our biotribology device. It was found that the Autologous Chondrocyte Implantation (ACI) method of cartilage repair developed by the Goteborg group gave less wear than that of "normal" cartilage from the same joint. In line with our previous experience, there is no correlation between cartilage wear and friction. Plans for further studies of biotribology are briefly outlined.

COLL 424 Gastric vs. sub-maxillary mucins: Contrasting pH effects on conformation and lubrication at a water/elastomer interface

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Mucins are high-molecular-weight (> 1,000,000 Da) glycoproteins that constitute the slimy mucus secretion covering epithelial cell surfaces and are known to be primarily responsible for the protective and lubricious properties of the viscoelastic mucous barrier. In this study, we compared the lubrication properties of mucins originating from different internal organs by employing bovine submaxillary mucin (BSM) and porcine gastric mucin (PGM). To emulate the ‘soft' contacts occurring in common physiological conditions, an elastomer possessing a low elasticity modulus (< 2 MPa), e.g. poly(dimethylsiloxane) (PDMS), has been employed as tribopair. Even though mucins generally reveal common structural features, for instance, partial glycosylation of linear polypeptide backbone and possible aggregation via hydrophobic or disulfide bonding, contrasting lubrication behavior was observed from BSM and PGM by changing the aqueous solution environments. A major difference between the two mucins is that BSM behaves as an excellent aqueous lubricant additive under neutral pH conditions (pH 7), losing this function under acidic conditions (pH 2). For PGM, however, effective lubrication was observed under acidic conditions (pH 2), while the lubrication effect was negligible under neutral conditions (pH 7). The contrasting pH effects on the lubrication properties of these two mucins are discussed in with the context of their structure and conformation at the water/PDMS interface.

COLL 425 Effect of glycoproteins on friction in diarthroidal joints and between model surfaces measured with lateral force microscopy

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Glycoproteins, such as lubricin, play a prominent role in the boundary lubrication mechanism in diarthroidal joints, where the superficial surface layer (SSL) of articular cartilage serves as the bearing surface. The loss or damage of the SSL likely initiates cartilage damage and often leads to joint diseases such as osteoarthritis. Although the tribological properties of the SSL are widely studied, the details of the boundary lubrication mechanism remain poorly understood. This is mainly due to the chemical and morphological heterogeneity of the cartilage surface. We measured friction by lateral force microscopy using chemically functionalized colloidal probes on model surfaces and cartilage from genetically engineered mice. First we present results of friction measurements between w-substituted alkane thiol modified model surfaces in presence of lubricin. We report on the friction effect caused by removing the O-linked b(1,3)Gal-GalNAc oligosaccharide side chains from lubricin. Finally, we report on in-situ friction measurements on cartilage obtained from lubricin-deficient mice.

COLL 426 Diamond-like-carbon coatings for dry machining of aluminum alloys

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Dry machining of aluminum is challenging because aluminum chips formed during machining can strongly adhere to the tool surfaces, causing tool failure. We show that diamond-like carbon (DLC) coatings are promising candidates for dry machining of aluminum because aluminum has much less tendency to adhere to DLC surfaces compared to other hard coatings. To better understand the tribological behavior of DLCs, we have recently conducted experimental studies of adhesion, friction, and wear of several DLC coatings against aluminum over a wide range of temperature and under various environments, including vacuum, argon, nitrogen, hydrogen, and ambient air. We found that hydrogen can have a strong effect on adhesion, friction, and wear of DLCs against aluminum. We have also investigated the effects of hydrogen and other species using density functional theory calculations of the work of separation at the aluminum-diamond interfaces. These findings provide helpful insights that can be used to further develop carbon-based coatings for dry machining of aluminum alloys.

COLL 427 Tribological and electrical properties of vertically aligned multi-walled carbon nanotubes

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This work examines the electrical contact resistance and tribological behavior of vertically aligned multi-walled nanotube (MWNT) films. A 250 micrometer long MWNT film and a gold sphere are actuated for 3000 hot electrical switching cycles. Under a 5 mA sourced current, the electrical contact resistance across the MWNT and gold interface remained approximately 42 ohms over all 3000 switching contacts, showing no degradation (resistance increase) with repeated switching. Reciprocating microtribological experiments are also performed to simultaneously examine the friction coefficient and electrical contact resistance at the sliding gold-MWNT interface. Hot electrical switching experiments and microtribological siding tests are repeated between a gold sphere and gold foil for contact resistance, friction coefficient and surface degradation comparisons. The closed

shell structure of the nanotubes may prevent electrical and chemical degradation at the interface making nanotube films viable candidates for continual hot electrical switching and sliding applications.

COLL 428 Elucidation of the atomic-scale mechanisms of friction in model SAMs and DLC films

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The development of micron-sized devices for terrestrial and space applications has prompted the need for protection of the surfaces of these devices. Amorphous carbon films, diamondlike carbon, and SAMs are all possible candidates for the passivation and lubrication of these devices. The fundamental problem associated with controlling friction is a lack of understanding of the underlying atomic-scale processes that govern it. Over the past several years, we have performed extensive molecular dynamics simulations aimed at understanding the atomic-scale mechanisms of friction. We have examined the contact forces present at the interface of a tip and SAMs during sliding. Compression- and shear-induced polymerization have also been modeled in SAMs. In addition, we have done simulations that analyzed the tribological properties of amorphous carbon films with various compositions and of diamondlike carbon films. Some of our recent results will be discussed.

Coworkers: P. T. Mikulski, G. Gao, K. Van Workum, G. Chateauneuf, J. D. Schall ** Work supported by AFOSR and ONR.

COLL 429 Atomic-scale insight into hydrodesulfurization catalysts

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Presently, there is worldwide focus on the production of transport fuels with very low sulfur contents. In order to produce ultra-low sulfur diesel (ULSD) meeting the new environmental specifications, one has to desulfurize refractory compounds like 4,6-dimethyldibenzotheophene (4,6-DMDBT). It has been known that such molecules may be desulfurized by two different pathways, i.e. a direct desulfurization (DDS) pathway and a hydrogenation (HYD) pathway but very limited information has been available regarding the nature of the sites involved in the reactions. Recently, such information has been provided by applying a variety of theoretical and experimental approaches. This insight has allowed one to obtain a molecular-level understanding of the reactions and has also elucidated important inhibition effects. The insight has also aided the development of new, high-activity industrial catalysts.

COLL 430 Catalytic chemistries for the conversion of dimethyl ether to oxygenates

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The emergence of dimethyl ether (DME) as a chemical intermediate has created opportunities for its conversion to useful products. The smaller amount of co-produced water (relative to methanol reactants) leads to products with higher purity and to weaker kinetic inhibition effects. Here, we report the selective oxidation of DME to formaldehyde on catalysts based on dispersed MoOx and VOx domains and the structural requirements for redox cycles involving lattice oxygens and limited by C-O bond cleavage. We also report the selective carbonylation of DME to methyl acetate on acidic zeolites. Kinetic, isotopic, and spectroscopic data are consistent with a sequence of elementary steps initiated by methylation of acid sites and limited by CO addition to the resulting methyl groups to form acetyl species, which then desorb as methyl acetate in fast methylation reactions without concurrent formation of water and with the re-formation of methyl groups.

COLL 431 Pareto-optimal methanation catalysts

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Using the methanation reaction as the example, we employ a model based on density functional theory calculations to screen a large number of alloys for catalytic activity. By including information about the cost of the constituents, we determine the Pareto optimal set of alloys which represent the best possible compromise between activity and price. The best catalysts were then synthesized and the catalytic activity measured. Ni3Fe and NiFe alloys are shown to be superior to the Ni catalysts used today both in terms of activity and cost.

COLL 432 Microkinetic analysis of catalyzed reactions: A means for gaining insights into the effects of catalyst composition on catalyst activity and selectivity

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An understanding how catalyst composition and structure influence catalyst activity and selectivity can provide guidance for the development of catalysts. To achieve this goal it is necessary to first determine the pathways via which reactions occur and determine the rate coefficient for each elementary step. With this information in hand, it is possible to develop an accurate representation of the overall dynamics not only under steady-state but also under non-steady-state conditions. Equally important, such microkinetic analysis can provide an appreciation for how changes in catalyst composition and structure influence the rates at which elementary reactions proceed, and not just the global kinetics. This talk will present several illustrations of the microkinetic analysis to both homogeneously and heterogeneously catalyzed reactions. Examples will include the epoxidation of olefins by hydrogen peroxide catalyzed by iron porphyrins, the selective oxidation of methane by isolated molybdate species, and the oxidation and oxidative carbonylation of methanol by Cu-containing zeolites. The importance of combining information from both experiments and theory will be demonstrated throughout the talk.

COLL 433 New insight in catalytic nanoparticles

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Nanoparticles may exhibit properties that are quite different from those of the bulk material. In metal oxide supported catalysts, support interactions may change both the chemical and the structural properties of the nanoparticles. Studies have shown that low-coordinated atoms (e.g. at edges and corners) have significantly different reactivity than atoms at the closed packed facets. It is apparent that if the metal oxide support influences the structure of the nanoparticles, favoring certain shapes, facets, or defect sites, this may have a dramatic effect on the catalytic activity. Similarly, the presence of low-coordinated sites may influence the deactivation of a metallic catalyst. These properties will furthermore depend on the environment that the catalyst system is exposed to. Thus, in situ investigations of the catalysts under realistic reaction conditions are needed since the structure and chemical state of the active catalyst usually is different from that found ex situ or post-mortem.

COLL 434 Surface reactions of complex epoxides on silver

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Epoxides react on silver via activated ring opening to form surface oxametallacycles. The simplest member of this family, a –CH2CH2O– species tethered to the surface at both ends, has been shown to be the key intermediate in the selective epoxidation of ethylene. Motivated by the successful epoxidation of butadiene by Monnier and co-workers, we have examined the chemistry of surface oxametallacycles formed from epoxybutene, styrene oxide, and isoprene oxide on low index surfaces of silver using both surface science and computational tools. In all cases the epoxides of conjugated olefins form oxametallacycles that are significantly more thermally stable than the corresponding structure derived from ethylene oxide. These more complex oxametallacycles react via different pathways to form epoxides as well as other oxygen-containing products. The reactivity patterns from surface science can be linked to the selectivity of complex olefin oxidations with silver catalysts.

COLL 435 Near-surface alloys for improved catalysis

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Periodic self-consistent Density Functional Theory (DFT-GGA) calculations have emerged as a valuable partner to experiment in explaining reactivity of transition metal surfaces. These methods provide detailed atomic level mechanistic information on individual elementary reaction steps, in terms of reaction thermochemistry, reaction paths, and activation energy barriers. Trends in reactivity derived from systematic investigations of specific steps on a number of different metal surfaces are reliable, when compared to experiment. In particular, we will attempt to demonstrate how first-principles methods can extend beyond the detailed mechanistic analysis of catalytic reactions to reach the ambitious goal of identifying promising catalysts for specific applications. Among others, we will discuss opportunities to design bimetallic catalysts for highly selective hydrogen transfer reactions, and for designing cheaper and more active oxygen reduction catalysts, the latter being most relevant to the cathode reaction of low temperature fuel cells.

COLL 436 Constructive lithography: A generic approach to the advancement of a viable bottom-up nanofabrication methodology

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A main challenge en route to a viable bottom-up nanofabrication methodology is the creation of a gradually evolving assembly framework that can reproducibly process and amplify chemical-structural information according to a preconceived plan, through a hierarchical sequence of template-guided self-assembly steps. Constructive Lithography, a generic chemical approach specially conceived for this purpose, combines processes of monolayer self-assembly and surface chemical modification with a nondestructive electrochemical patterning technique carried out with the assistance of a conductive AFM tip or a conductive stamp. This allows the deliberate assembly of a large variety of planned 3D supramolecular architectures on silicon, spanning the lateral dimension range from nanometer to millimeter. Examples will be given to illustrate some of the unique capabilities offered by this approach in the fabrication of surface architectures combining diverse organic and inorganic materials, on different length scales.

COLL 437 Positioning single molecules on protein-resistant surfaces

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The ability to control the nanoscale location of individual bio-molecules on bio-compatible surfaces will open up new possibilities for biological research at nanoscale. Towards this goal, we have

developed a robust system based on oligo(ethylene glycol) (OEG) monolayers grown by hydrosilylation of OEG-terminated alkenes on hydrogen-terminated silicon surfaces. These films prepared under optimized conditions nearly eliminated the non-specific adsorption of a wide variety of proteins. We demonstrated that these ultra-flat monolayers can be locally oxidized under a biased AFM tip to generate patterns presenting carboxylic acid groups for anchoring large molecules. We have achieved a pattern resolution similar to 10 nm – close to the size of large, adsorbed protein or dendrimer molecules. The preparation of arrays of such single molecules and the subsequent studies will be presented.

COLL 438 Designing nanopatterned surfaces for biomolecule adsorption using automated scanning probe lithography

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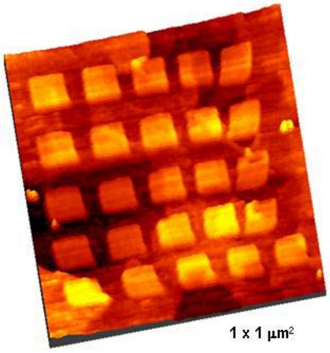
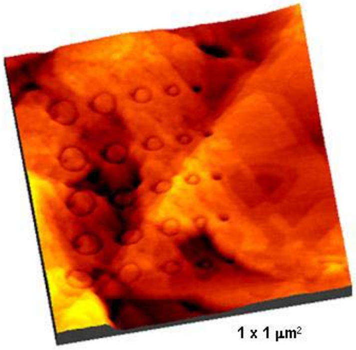
Molecular-level studies which combine nanoscale lithography with AFM characterization are used to investigate biomolecular surfaces. Scanning probe lithography offers nanoscale precision for fabricating well-defined regions of surfaces with reactive or adhesive ligands for attaching proteins. Automated SPL can rapidly fabricate arrays of nanopatterns of functionalized alkanethiols with designed terminal chemistries. Nanografting enables superb control of spatial parameters such as ligand density for elements of nanopatterned arrays. Example AFM topographs are shown below for a 5 x 5 array of 100 nm squares of hexadecanethiol written in a glucosyldithiol matrix; and for a series of smaller rings of glucosyldithiol written within a hexadecanethiol monolayer. Nanopatterns of self-assembled monolayers (SAMs) can be selected to present reactive groups (such as aldehyde or carboxylate) for binding proteins. Height changes are used to monitor successive surface changes with protein adsorption during in situ experiments, furnishing information regarding protein orientation and the selectivity and efficiency of SAMs for binding biomolecules to surfaces.





COLL 439 Application of nanoimprint technology in protein patterning and nano-SPR sensors

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Selective localization of active proteins to patterns or specific sites is important for development of biosensors, bioMEMS, and basic proteomic research. One of our efforts is to integrate motor proteins in microfabricated devices to create molecular sorters powered by biochemical energy. Biomolecular motor proteins are nanoscopic engines that utilize the free energy from the hydolysis of ATP molecules to move along microtubules. We developed a technique to create nanotracks-integrated microfluidic channels to guide the motion of microtubules (MTs) that are propelled by immobilized kinesin motor proteins, and demonstrated separation of antibody analytes from the flow region.

We are also developing a label-free and compact optical nanobiosensor that is based on the surface plasmon resonance of metallic nanoparticles. Nanoimprinting technology is exploited to create large areas of metallic nanostructures with controlled shape, size and spacings in order to evaluate important design issues in optimizing such nano-SPR sensors.

COLL 440 Selective placement of templated DNA nanowires between microstructured electrodes

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We report the deposition of polyelectrolyte films between microfabricated electrodes as a selective guide for DNA templated nanowire structures. Dip-pen nanolithography (DPN) was first used to fabricate a layer of positively charged polyelectrolyte, poly(allylamine hydrochloride) (PAH), on a spin-on silicon oxide surface between gold electrodes. Further deposition was done with a negatively charged polyelectrolyte, poly(styrene sulfonate) (PSS), on top of the PAH film. The functionalized architecture was used as a scaffold to stretch DNA wires coated with positively charged magnetic nanoparticles. Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Force Imaging and Adhesion Mapping were used to verify the deposition of the polyelectrolyte films between the microfabricated gold electrodes. From these experiments we have concluded that the selective deposition of polyelectrolyte films can be effectively incorporated into microfabricated devices for the guided assembly of DNA templates. Prototype device structures were tested and the formation of nanometer scale gaps on the DNA wires was explored using restriction enzyme digests. This work can become the basis for novel (bio)sensor architectures.

COLL 441 Directed self-assembly of virus particles at chemical templates

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Because viruses can be engineered site-specifically to present catalytic, electronic, and optically active moieties, they are attractive as nanoscale building blocks for hierarchical structures. We report results using scanned probe nanolithography to direct organization of viruses into 1D and 2D patterns and in situ AFM imaging to investigate the dynamics of organization as pattern geometry, inter-viral potential, virus flux, and virus-pattern interaction are varied. Icosahedral Cowpea Mosaic Virus and wire-like bacteriophage were modified to present surface sites with histidine (His) tags or anti-strepavadin (AS) motifs, respectively. Flat gold substrates were patterned with 10-100nm features of alkyl thiols terminated by nickel-chelating nitrilotriacetic acid or biotin to bind to the Hys and AS groups, respectively. AFM imaging showed that assembly kinetics, degree of ordering and cluster-size distribution at these templates depended on all the parameters and gave 1D and 2D arrays and 2D films. We present a physical picture of virus assembly at templates that incorporates nucleation dynamics of small-molecule epitaxial systems and condensation dynamics of colloidal systems. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

COLL 442 Surface modification through recognition mediated orthogonal self assembly of polymer and nanoparticle

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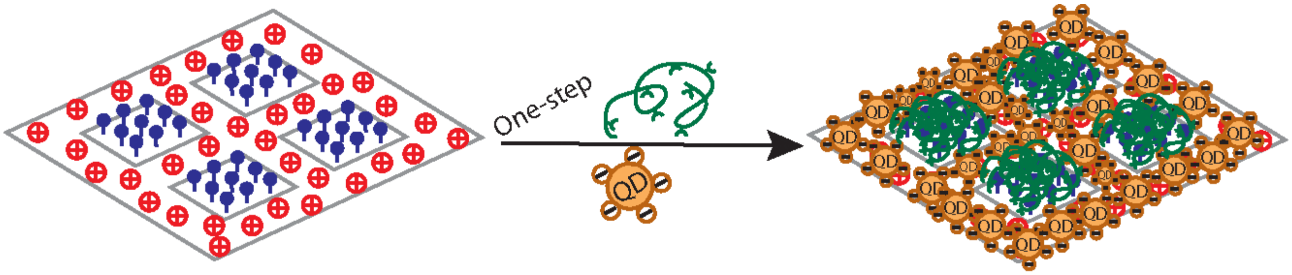
The development of engineered microscopic surface structures and miniaturized systems for chemical, analytical, and diagnostic applications are of interest in many areas of science and technology. We present a methodology here by integrating photolithography and orthogonal self-assembly concept together for complex surface modification. Orthogonal self-assembly demonstrates the potential of rapid, simultaneous, and site-selective adsorption of molecules and mesoscopic objects at pre-patterned regions using different noncovalent supramolecular interactions. Herein, we report the patterning of silica surfaces with thymine (Thy) and positively charged N-methylpyridinium (MePy) in microscale using photolithography and the subsequent orthogonal modification with diaminopyridine functionalized polystyrene (DAP-PS) and carboxylate derivertized CdSe nanoparticle (COO-NP) through DAP-Thy three-point hydrogen bonding and MePy-COO electrostatic interactions, respectively. This two-component orthogonal surface modification can be finished in a self-sorting, single-step fashion.



COLL 443 New methods for imaging chemistry

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I will describe the progress of our work to develop powerful new approaches to optically characterizing complex molecular interactions on surfaces. The foundations of this effort are rooted in the properties of plasmonic microstructures, sub-wavelength optical devices that provide unique capacities for imaging chemical phenomena on surfaces. New methods of soft-lithography, in combination with surfaces modified via self-assembly, provide a low cost pathway to devices that hold considerable potential to transform chemical sensing. Examples of bioanalytical assays and more complex dynamical sensors will be described.

COLL 444 Single-molecule probing of binding events to g-protein coupled receptors

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G-protein coupled receptors are the targets of most pharmaceuticals, yet the kinetics of the binding events, the structures of these integral membrane proteins, and the ligand-induced conformational changes are largely unknown. Single-molecule spectroscopy offers a unique opportunity to obtain unprecedented information along each front. Adsorption-desorption kinetics of enkephalins labeled with dye are probed, along with orientational states of the dye, as these drugs adsorb and desorb to delta-opioid receptors in supported lipid bilayers and in neuronal cells.

COLL 445 Differential measurements of the mechanical and electrical properties of the bio-molecules using AFM-based techniques

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The applications of scanning probe microscopy (SPM) to surface science are, of course, countless and have brought a real revolution to the field. Less expected but, a posteriori, equally logical is the revolution that single molecule experimentation (with both SPM and other probes) is bringing to the study of macromolecules of both biological and non-biological origin. On the other hand, in this journey towards single molecule studies it is actually at present possible to choose the size of the sample rather freely. Each size (1 or 1,000 or 1,000,000 molecules or even the bulk) has its own advantages and drawbacks both experimentally and theoretically. I hope to show evidence from our own laboratory that working at the hundreds of molecules level, presents some unique advantages that make this type of experiments well worth pursuing. After having introduced the methods that give us the possibility to isolate a sample on the order of 100 to 1,000 molecules in the middle of a reference (larger) set of similar molecules, I will apply the time honored method of differential measurements to study the properties of monolayers of molecules of increasing complexity. Both electron tunneling and mechanical measurements will be discussed. In the former I will compare the "conductivity" of saturated hydrocarbons with aromatic ones, while in the latter the compressibility of "incompressible" artificial proteins patches will be compared with that patches of "compressible" proteins that are structurally less stable.

COLL 446 Applications of oxidase modified electrodes

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The reactions of cytochrome c oxidase (CCO) from both mammalian (bovine) and yeast (*B. stearothermophilus*) sources immobilized in electrode supported bilayer membranes have been studied. The kinetics of oxidation of reduced cytochrome c at immobilized CCO under flow injection conditions mimics known rates. CCO exhibits electron transfer kinetics with reduced cytochrome c that are non-hyperbolic and consistent literature properties of these enzymes *in vitro*. The Michaelis high and low affinity binding constants are about 10 µM and 120 µM, respectively, also consistent with literature reports *in vitro*. These structurally different CCO molecules assemble into electrode supported bilayers in functional states, are stable up to 80^{o}C, and remain active for weeks. Mammalian respiration is disrupted by toxic agents such as cyanide by binding to CCO. Ferrocytochrome c oxidation and oxygen reduction by CCO are inhibited upon cyanide binding. Cyanide binding was found to be reversible enabling analysis of serially injected cyanide samples of varying concentration. Binding constants (K_i) were determined for binding of cyanide to the reduced (62 µM) and oxidized (195 µM) forms of CCO. The response of CCO to cyanide is stable over a period of 10-14 days. Monitoring of the ambient redox potential in patients undergoing resuscitation from hemorrhagic shock is being examined as a clinical diagnostic for recovery. The CCO-modified electrodes described here have been shown to respond potentiometrically to the redox state of cytochrome c samples. Possible application as a clinical sensor for detecting when the electron flow through the respiratory chain is blocked is being considered.

COLL 447 Direct ethanol fuel cells: A chemist's challenge

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The proton exchange membrane (PEM) direct ethanol fuel cell (DEFC) presents a variety of chemical challenges not previously encountered in PEM type cells. This cell has the potential to provide good energy density, if electrocatalysts are found that efficiently carry out the 12-electron oxidation of ethanol to carbon dioxide and water. Unlike electrocatalysts presently utilized in fuel cells, an ethanol catalyst must efficiently cleave carbon-carbon bonds while adding oxygen atoms to the substrate. Presently available catalysts tend to stop at acetaldhyde or acetic acid products leaving the C-C bond intact. The present work evaluates a series of metal on metal oxide supported catalysts under actual fuel cell conditions as electroactive interfaces for the DEFC. A polyol procedure is used to synthesis a variety of nanoparticulate group 10 metal on tin oxide or rare earth oxide supports. These electrocatalysts are characterized in single cell PEM fuel cell test fixtures using electrochemical techniques, electron microscopy and product analysis. The exact morphology of the catalyst along with the operating temperature of the fuel cell are found to be key mechanistic parameters.

COLL 448 Self-assembling of aqueous polyelectrolytes: Polyelectrolyte complex particles and micellar structures

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Two types of polymeric self-assemblies will be discussed. The first one comprises complexes of polyelectrolytes with opposite charges. As is well known the complexes with the anion/cation ratio close to unity turn hydrophobic and precipitate from aqueous solutions. We have managed to prepare anionic diblock copolymers with short poly(ethyleneoxide), PEO, blocks, as well as polycations grafted with relatively short PEO chains. Using these polymers it has been possible to obtain colloidally stable amphiphilic complex particles. An interesting finding is that the complex particles are typically very monodisperse, and clearly tend to form particles with a certain optimal size regardless of the molar mass of the polymers. The complex particles are in a dynamic equilibrium: chain exchange between the dispersed entities takes place continuously. The kinetics and mechanism of the chain exchange has been studied using fluorescence spectroscopy. Fluorescence labeling of the polymers has also enabled the investigation of the overcharging of the complexes. The other type of polymers to be discussed is star diblock copolymers. Diblock stars with four arms have been prepared, where the inner block is hydrophobic poly(methyl methacrylate) and the outer one is poly(acrylic acid). These are polymers with an extremely complicated behavior when dissolved in water. Semidilute solutions tend to gelate, they form fragile gels which break upon shear. In dilute aqueous solutions, a tendency to aggregate into spherical micelles may be observed and upon addition of salt, wormlike micelles build up. The very delicate balance between electrostatic and hydrophobic interactions in this case has been experimentally studied by changing the relative lengths of the hydrophobic and hydrophilic blocks. In addition, molecular modeling by computer simulations has been initiated and the first results are promising: it seems we can e.g. predict the ionic strength where the worm-like micelles build up.

COLL 449 Stimuli-responsive polymers prepared by living radical polymerization

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Novel water-soluble block copolymers that respond to physical and chemical external-stimuli were prepared by reversible addition-fragmentation chain transfer (RAFT) and by organotellurium-mediated living radical polymerization (TERP). TERP is particularly useful for the controlled polymerization of water-soluble nonconjugated vinyl monomers including *N*-vinylpyrrolidone. The molecular weight distribution (M_w/M_n) of poly(*N*-vinylpyrrolidone) (PVP) prepared by TERP was found to be narrower than that prepared by RAFT radical polymerization. PVP prepared by TERP can initiate polymerization of a second monomer, e.g., *N*-isopropylacrylamide, and thus a thermo-responsive block copolymer, PVP-*block*-PNIPAM can be prepared. This block copolymer dissolves molecularly in water at room temperature but it collapses into a micelle-like aggregate with hydrophobic PNIPAM cores and hydrophilic PVP coronas above its lower critical solution temperature (LCST). Synthesis, characterization and properties of this and other stimuli-responsive block copolymers will be detailed in the presentation.

COLL 450 Amphiphilic copolymers containing single-stranded DNA for single-base mutation assay

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We developed a reliable method for detecting single nucleotide mutation by using spontaneous aggregation of a DNA-carrying colloidal nanoparticle, which was composed of a hydrophobic core from poly(N-isopropylacrylamide) (polyNIPAAm) and a hydrophilic shell from probe DNA. The particle with the diameter of 50 nm was formed through self-assembly of polyNIPAAm-graft-DNA copolymers above the phase transition temperature of polyNIPAAm part. When adding the complementary DNA into the colloidal dispersion, the particles were found to aggregate rapidly in buffer (pH 7.4) containing 0.5M NaCl through a non-crosslinking mechanism. In contrast, they kept dispersing in the presence of the one point-mutated DNA under the identical conditions. When using capillary electrophoresis (CE), sequence-specific DNA separation was attained based on a difference in affinity of sample DNAs with a probe DNA which was chemically anchored to water-soluble nonionic polymers such as polyacrylamide and PEG. By the miniaturization using a microchip made of polydimethylsiloxane, we have succeeded in much faster separation than the conventional CE apparatus.

COLL 451 Oxidation-induced micellization of a diblock copolymer containing stable nitroxyl radicals

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Oxidation-induced micellization was attained for a diblock copolymer containing 2,2,6,6-tetramethylpyperidine-1-oxyl (TEMPO). Poly(4-vinylbenzyloxy-TEMPO)-block-polystyrene (PTEMPO-b-PSt) formed spherical micelles in carbon tetrachloride, a nonselective solvent by the reaction with chlorine. UV and ESR analyses demonstrated that the micellization occurred through the oxidation of the TEMPO by the chlorine to insoluble oxoaminium chloride (OAC), the one-electron oxidant of TEMPO. The resulting POAC-b-PSt micelles served as a one-electron oxidizing agent for N,N,N',N'-tetramethyl-1,4-phenylenediamine to produce Wurster's blue chloride, reverting themselves to the PTEMPO-b-PSt unimers. The micelles also acted as a two-electron oxidizing agent for benzyl alcohol to benzaldehyde. In this oxidation, no dissociation of the micelles occurred because the OAC was converted to the insoluble hydroxylamine-hydrochloride salt.

COLL 452 Influence of the hydrophobic monomer on the behavior of HASE rheology modifiers

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Although HASE (Hydrophobically Modified Alkali Swellable Emulsions) have been known for a long time, little attention as been paid to the hydrophobic monomer responsible for the characteristic intermolecular aggregation. In this study, we investigated the impact of the structure and nature of the hydrophobe on the properties of HASE solutions. Significant differences have been observed in terms of rheology profile (pseudoplastic to Newtonian), viscoelasticity and, interestingly, resistance of viscosifying effect toward added surfactants. In addition, the viscosifying effect has been studied in various paint latexes. These measurements highlight a large influence of the latex composition on the rheology profile of the blend.

COLL 453 Interfacial behavior of polystyrene-*block*-poly(*t*-butyl acrylate) star copolymers

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The self-assembly of several polystyrene-*block*-poly(*t*-butyl acrylate) sixty-four-arm star copolymers was studied at the air-water interface. The block copolymers consist of a polystyrene (PS) core and a poly(*t*-butyl acrylate) (PtBA) corona. The PS molecular weight remains constant (48 repeat units per arm), whereas the PtBA chain length varies from 104 to 445 repeat units. The Langmuir monolayers were analyzed performing Π-A isotherms and the Langmuir-Blodgett films morphologies were studied by Atomic Force Microscopy (AFM)**.** The Π-A isotherms exhibited a plateau around 24mN/m with a length that is highly dependant on the molecular weight. The plateau suggests a rearrangement of the polymer chains as the film is compressed. The Langmuir-Blodgett films were prepared by transferring the Langmuir monolayers onto mica substrates for different surface pressures. While surface micelles formed spontaneously at low surface pressure, AFM analysis above the plateau revealed the aggregation of those initial micelles into bigger domains.

COLL 454 Non-surface active ionic amphiphilic block copolymers: Special characteristics and micellization

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The ionic amphiphilic block copolymer is a novel substance since it shows characteristic properties which ionic low-molecular weight surfactants nor non-ionic block copolymers do not have. The ionic amphiphilic block copolymers show no surface activity, i.e. no surface tension reduction and no or few foam formation, but they form micelles in water. The origin of the non-surface activity can be attributed to the contribution of image charge effect at the air/water interface, which exceeds the hydrophobic adsorption. In this sense, this special characteristic is produced by the balance of “ionicity”, “hydrophobicity” and “polymerity”. In other words, the superposition of these three characters does not produce a just a sum of these three but produce novel properties. Micellization behavior is also different from other conventional low-molecular weight surfactants and block copolymers: the critical micelle concentration (cmc) “increases” with added salt concentration in contrast to the well-known Corrin-Harkins law. In addition, cmc decreases with increasing hydrophobic chain length, but turned to increase with further length increase, which is also contradict to the normal surfactant behavior. The micelle size and shape were not influenced by salt addition up to 10^-1 M, which is anomalously high salt concentration. The sphere to rod transition of the micelle was observed by further addition of salt. In addition, a large aggregate was observed by dynamic light scattering in addition to the translational diffusion of micelle particles even below the cmc determined by hydrophobic dye solubilization method. References (1) P.Kaewsaiha, K.Matsumoto, H.Matsuoka, Langmuir, 21(22), 9938 - 9945 (2005). (2) H.Matsuoka, S.Maeda, P.Kaewsaiha, K.Matsumoto, Langmuir, 20(18), 7412-7421 (2004). (3) H.Matsuoka, M.Matsutani, E.Mouri, K.Matsumoto, Macromolecules, 36(14), 5321 – 5330 (2003).

COLL 455 Interactions between amphiphilic biopolymers and vesicles

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This talk will describe our work on mixtures of an amphiphilic biopolymer with unilamellar vesicles formed from surfactants or lipids. The polymer we employ is a chitosan to which we graft hydrophobic (n-alkyl) side chains. When mixed with vesicles, the polymer hydrophobes tend to embed in vesicle bilayers, leading to the bridging of adjacent vesicles by polymer chains. This results in an increase in fluid viscosity and eventually to an elastic gel, where the vesicles are interconnected into a 3-D network. We use a combination of rheological techniques, small-angle neutron scattering

(SANS) and cryo-transmission electron microscopy (cryo-TEM) to investigate these vesicle-polymer mixtures. Variables of interest include the length of hydrophobic side chains, the graft density of hydrophobes, and the polymer molecular weight. The systematic influence of these variables on the structure and rheology of the resulting samples will be explored.

COLL 456 Acid-base tribochemical reactions under boundary lubrication

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Acid-base reactions governed the antiwear and friction reducing performance of additives under boundary lubrication conditions. Hard acid-hard base reactions explain how abrasive metal oxide debris are chemically eliminated by organic polyphosphate or borate species under pressure and stress. Soft acid-soft base reactions occur when nascent metal surfaces are produced in extreme pressure conditions. The metal surfaces immediately react with organic sulfides, chloride or fluoride species to passivate the surface and prevent the surfaces from adhesive wear and scuffing. These reactions have been successfully modelized. We show here two approaches. The first one is based on the use of an ultrahigh vacuum analytical tribometer in which specific and model surfaces are allowed to slide on each other and XPS/AES analyses shows the chemical reactions. The second is a numerical approach using Molecular Dynamics calculations. Both approaches gave similar results and well reproduced the tribochemical reactions at the macroscale.

COLL 457 Understanding the tribological chemistry of chlorine- and sulfur- and phosphorus-containing additives

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Chlorine- and sulfur- and phosphorus-containing compounds are added to the base fluid to synthesize extreme-pressure (EP) lubricants. The surface chemistry lubricant additives is studied in ultrahigh vacuum. Similar reactions are carried out at higher pressures using a microbalance where film growth rates are measured from the change in sample mass. Both the nature of the surface film and the reaction activation energies are identical in both regimes where chlorine-containing EP additives decompose forming films of iron chloride ($FeCl_2$) or carbide (Fe_3C), and that dialkyldisulfides react to form FeS and Fe_3C. These results, when combined with wear data, can be used to model the EP behavior of model lubricants by assuming that the film acts to prevent seizure, and that seizure occurs when the film is completely removed. The tribological properties of evaporated and reactively grown thin films are investigated in ultrahigh vacuum to correlate film properties with their tribological behavior

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COLL 458 Pressure induced transformation of ZDDP films

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Lubricants for automobile engines often include additives such as zinc dialkyldithiophosphates (ZDDPs). ZDDPs are known to break down on surfaces sliding in contact to form antiwear films comprised of polyphosphate glasses. Automobile manufacturers would ideally like alternatives to

ZDDPs due to the harmful effects of the phosphorus and sulphur derivatives on the catalytic converter. Furthermore, the inability of ZDDPs to protect aluminum surfaces has limited their use in aluminum engines, which are of considerable interest as fuel efficient replacements for steel engines. The antiwear film protects steel and cast-iron surfaces within an engine from wear. Although ZDDPs have been used for more than 60 years, there is still much to learn about the physical and chemical processes responsible for the formation and function of antiwear films. Little is currently known at the molecular level about the transformation or mechanism of action of the antiwear films, but a recent theoretical simulation has proposed that under the high-pressure conditions in an engine, zinc phosphate undergoes polymerization into a hard, cross-linked network connected through the zinc atoms. We are directly testing this concept by applying the pressures predicted by theory to films of ZDDP spin-coated onto steel surfaces, followed by studying the chemical nature of the films through various surface sensitive spectroscopic analytical methods (XANES and X-PEEM) prior to, and subsequent to the applied pressure regimes.

COLL 459 Spectromicroscopy studies of tribochemistry: X-PEEM characterization of self-mated wearing in humidity-controlled environments for ultrananocrystalline diamond and tetrahedral amorphous carbon

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In this study, tetrahedral amorphous carbon (ta-C) and ultrananocrystalline diamond (UNCD) films were subjected to fretting wear experiments in air and dry N2 with fixed relative humidity values of 0% and 50%. Friction was measured during fretting and the wear tracks examined with both atomic force microscopy (AFM) and X-PEEM-XANES (X-ray PhotoElectron Emission Microscopy combined with X-ray Absorption Near-Edge Structure) spectromicroscopy. The primary goal was to determine if X-PEEM could discern chemical differences between the wear track and the unworn film. An initial analysis showed that not only could X-PEEM show chemical differences in the wear tracks, but that they were distinct enough to lead to the quantitative interpretation of the changes in the bonding structure due to wear. Thus, these measurements give information regarding the wear mechanisms. Studies performed with a Si3N4 slider on ta-C (0% humidity) showed extremely low friction. According to X-PEEM, a weakly bonded carbonaceous layer that initially covers the ta-C film is scraped to the edges of the track. Surprisingly, this leaves high-quality ta-C inside the wear track and creates graphitized and oxygenated debris piles at each end. Similar experiments on UNCD showed oxidation of carbon in the wear track when oxygen was present in the environment. Experiments where the humidity level in a dry N2 environment is varied in smaller increments will also be discussed. Similar fretting studies were performed on self-mated UNCD and ta-C surfaces with equivalent loading parameters. We will discuss changes observed in both friction and the chemical signature of the surface as the amount of oxygen in the environment is varied. We will also discuss the relation between the amount of oxygen in the environment and the level of graphitization that occurs in the wear track.

COLL 460 Nanomechanics and tribology of coatings

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At all scales -- from atomically thin surface films to large wear debris particles – interfacial mechanics and dynamics play an important role in friction and wear. To study these processes we are combining several approaches: 1) in situ macroscopic tribological studies allowing visualization and chemical analyses of the buried interface, and 2) microtribology and nanomechanical measurements using scanning nanoindentation. Using these techniques, we are investigating the role of interfacial films on sliding at macroscopic and microscopic scales. For many solid lubricants, macroscopic tribological behavior is correlated with heterogeneous films, e.g. the “third bodies” found in the sliding interface. I will discuss “how” third body films form on the stationary counterface, “what” are their composition and mechanical properties, and “why” they provide low friction and prevent wear. I will give examples of from MoS2 and DLC based solid lubricated contact demonstrating the role that transfer films play in controlling friction behavior at macro- and microscopic scales.

COLL 461 Theoretical and experimental studies of ester surface chemistry on carbides

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Chemical interactions between mechanical component surfaces and lubricant or additive molecules play a vital role in preventing high friction and wear under boundary contact. To model these interactions, we have been performing theoretical and experimental studies of small ester molecules on the (100) surfaces of titanium and vanadium carbides. The carbides are important tribological materials, used as hard coatings on steel bearing surfaces and as hardening agents in steels. Esters are an important functional group in aerospace lubricants, and are typically more reactive with surfaces than are simple hydrocarbons. In this work, we compare the results of density functional theory (DFT) calculations of the bonding and reaction of the simplest ester, methyl formate, with experimental results obtained from surfaces analysis techniques such as HREELS and XPS. We find that the DFT work has helped to identify surface reaction products and is promising for the study of larger molecules that may not be practical to study experimentally.

COLL 462 Tribochemistry and tribopolymerization

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The concept of "in situ" surface polymerization as a mechanism of boundary lubrication was described in an article in Wear by Furey over 30 years ago in 1973. Since then, more particularly during the past 20 years, additional fundamental research has been carried out on this mechanism—referred to now as tribopolymerization— by Furey, Kajdas, Kempinski, Molina, Vick and several graduate students in the Tribology Laboratory at Virginia Tech. We define tribopolymerization as the planned, intentional, and continuous formation of protective polymeric films on tribological surfaces by the use of minor concentrations of selected monomers capable of forming polymer films "in situ" by polycondensation or addition polymerization. This paper reviews the key elements of our research, including the orientation of monomers on solid surfaces, and the importance of high surface temperatures and triboemission of low-energy electrons in inititating surface polymerization.

COLL 463 Thermal stability of covalently bound monolayers on porous silicon

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Covalently bound alkyl monolayers have been proposed as lubrication layers in microelectromechanical systems (MEMS) based on silicon. These monolayers must be stable in air at the high temperatures that could be generated by friction. The goal of our research is to investigate

the thermal stability of alkyl monolayers on silicon using as realistic conditions as possible. Alkyl monolayers were produced on stain-etched porous silicon using a 1:10 mixture of ethylaluminum dichloride catalyst to alkene, reacted at room temperature overnight under nitrogen. For the first time, the thermal stability of alkyl monolayers on this high-surface-area silicon has been measured in air using conventional thermal gravimetric analysis (TGA). For an octadecyl monolayer, decomposition or desorption occurs at 250 °C, confirmed by the absence of hydrocarbon peaks in transmission FTIR after TGA.

COLL 464 Hydrogen and chemicals from fossil and renewable fuels

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Autothermal reactors have great promise for hydrogen and chemicals production because they have reactor residence times of 10-3 seconds and require very simple reactors. We describe the production of hydrogen and olefins from fossil fuels from methane to diesel and from renewable fuels such as ethanol and biodiesel in millisecond reactors. For successful vaporization and mixing of heavy fuels the use of fuel injectors for rapid vaporization and mixing is essential to suppress flames and carbon formation. For ethanol to hydrogen we obtain 80% selectivity to hydrogen at nearly 100% conversion of ethanol and oxygen for an ethanol-air feed. By adding water we obtain 110% (H2 from ethanol and water) in a single stage reactor and 130% H2 selectivity in a staged reactor where a cooler section undergoes the water gas shift reaction. For biodiesel (the methyl ester of C18 fatty acids from soy oil), we can obtain 80% H2 selectivity at C/O=0.8 and 80% selectivity to olefins at C/O=1.5. At higher C/O ratios the ester linkage also survives to produce olefinic esters. Modeling with detailed surface and homogeneous chemistry is used to simulate and understand these processes.

COLL 465 Commercialization of aqueous-phase reforming: Challenges and progress

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Virent Energy Systems, Inc. is commercializing the Aqueous Phase Reforming (APR) process that allows the generation of hydrogen-rich gas streams from biomass-derived compounds such as glycerol, sugars, and sugar alcohols. The utilization of biomass-based compounds allows the APR process to be a carbon neutral method to generate hydrogen. In the near term, the feed-stock of interest is glycerol that is being generated as a byproduct in the production of biodiesel. Virent has developed the APR system for on-demand generation of hydrogen-rich fuel gas from either glycerol or sorbitol (the sugar alcohol formed by hydrogenation of glucose) to fuel a stationary internal combustion engine driven generator (5 kW). Virent is also developing the APR process for on-demand generation of hydrogen for small PEM or SOFC fuel cells (less than 500 watts). Additionally, Virent is currently developing the APR process to generate high yields of hydrogen from corn-derived glucose.

COLL 466 Renewable liquid alkanes from aqueous-phase processing of biomass-derived carbohydrates

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Fuels derived from biomass can alleviate environmental and political problems caused by our dependence on fossil fuels. We have developed highly efficient aqueous-phase catalytic processes for conversion of biomass-derived sugars into alkanes ranging from C1 to C15. Aqueous phase dehydration/hydrogenation (APD/H) of sorbitol (hydrogenated glucose) yields lighter alkanes ranging

from C1 to C6 by a bi-functional pathway involving dehydration with a solid (SiO2-Al2O3) or a mineral (HCl) acid catalyst followed by hydrogenation with a metal catalyst (Pt or Pd). Larger liquid alkanes in the diesel fuel range (C7-C15) can be produced by combining the APD/H process with an aqueous-phase aldol condensation step. Large water soluble organic molecules form during the aldol condensation step, which are then converted into liquid alkanes during APD/H. The alkane products retain approximately 95 % of the heating value and only 30 % of the mass of the biomass-derived reactants.

COLL 467 Heterogeneous catalysts for biorenewable conversion

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For biorenewable feedstocks to serve as a significant source of chemicals and/or fuels it will likely require the development of new chemical processes as well as biological processes. However, the conversion of biorenewable feedstocks with heterogeneous catalysts provides new challenges in chemical catalyst research and development relative to historical work with petrochemical feedstocks. These challenges include the need to selectively convert highly functionalized molecules and to perform efficient reactions in the condensed phase in which the liquid phase is commonly aqueous. The creation of selective heterogeneous catalysts in these systems will likely require tight molecular control of the catalytic domain. Presented will be results on the use of organic-inorganic hybrid catalysts based on mesoporous silicas in the esterification of fatty acids and the hydrolysis of oligosaccharides. These reaction systems will be used to demonstrate the importance of active site selection, pore diameter size, hydrophobicity/hydrophilicity of the catalytic material, spatial location of the active sites, and solution effects on the catalyst performance.

COLL 468 Thermodynamic investigation of the redox properties of ceria-zirconia solid solutions

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The thermodynamic properties of solid solutions of ceria and zirconia with varying compositions were studied as a function of temperature and oxygen fugacity. Equilibrium isotherms were determined for temperatures between 873 and 1173 K, using TPR methods and Coulomb Titration; and enthalpies and entropies of oxidation were determined. The thermodynamic properties were found to be a strong function of composition but were independent of sample surface area and calcination temperature, so long as the oxide structure was maintained. The redox properties of ceria-zirconia solid solutions were found to be substantially different from those of pure ceria or zirconia.

COLL 469 Use of dirty hydrogen in solid-oxide fuel cells

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Currently most fuel cells operate with hydrogen as the fuel, and require a reforming step upstream of the fuel cell to convert a hydrocarbon fuel into hydrogen, and to remove contaminants such as sulfur. The efficiency of the entire process would be improved if the fuels could be reacted directly in the fuel cell with no pretreatment. One of the difficulties with reacting hydrocarbons at high temperatures over current Solid-oxide Fuel Cell (SOFC) anode catalysts (typically Ni/YSZ) is the propensity for carbon formation. Our group is studying the interaction of hydrocarbons and sulfur with SOFC anodes, in order to better understand the mechanism of coke formation and sulfur poisoning, with the goal of designing improved anode materials. Studies are continuing to determine the effects of applied potential, of additional catalyst layers within the anode compartment, and of sulfur in the feed stream on the deactivation of the Ni anodes.

COLL 470 Formation, characterization and interfacial properties of random copolymers with adjustable monomer sequence distributions

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We describe the formation of A/B random copolymers with adjustable monomer sequence distributions and characterize their molecular properties and adsorption characteristics at polymer/substrate interfaces. The method (inspired by computer simulation studies of Khokhlov and coworkers) consists of first adjusting the degree of collapse/expansion of a homopolymer made of A units and reacting selected A monomers on the homopolymer with a “coloring” species B. By using polystyrene (PS) as a parent homopolymer and utilizing electrophilic substitution/addition of bromine in the para position of the phenyl ring of PS, a series of poly(styrene-co-4-bromostyrene) (PBrxS) copolymers with adjustable mole fraction (x) and sequence distribution of 4-bromostyrene (4-BrS) monomers in PBrxS are synthesized various halogen-alkane solvents, whose Theta temperatures for a given PS/solvent system range from 7 to 57 degrees C. The degree of bromination and the 4-BrS sequencing is controlled by varying the bromine concentration in the reaction vessel, bromination reaction time, and solvent temperature. Electro-optical Kerr effect measurements confirm that depending on the degree of collapse (poor solvent) or expansion (good solvent) of PS, the monomer sequence distributions in the resulting PBrxS range from blocky (poor solvent) to random (good solvent). We demonstrate the effect of the monomer sequence distributions in PBrxS on interfacial behavior of these random copolymers by: 1) performing dewetting studies of thin PBrxS films from solid surfaces, and by 2) utilizing adsorption-based interaction chromatography under various solvents conditions and chemistry of the stationary phase.

COLL 471 Defined surface architectures for biochips: Towards high throughput chip analysis

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One of the key problems in the development of a DNA chip for a given analytical problem is the determination of suitable experimental parameters (probe sequences, buffer,hybridization temperatures). As a consequence, development and optimization of a chip requires thousands of experiments and test chips leading to often unacceptable development times and costs. In this contribution we will present a chip platform that addresses this problem. A key feature of this system is the chip itself. We have developed a polymer chip made from PMMA or cyclic olefin copolymers (COCs) onto which the probes are printed together with a photocrosslinkable polymer. Upon illumination the polymer forms a three dimensional hydrogel that acts as a carrier for the probes. We describe how the resulting chips are used to generate complex microarrays, which are read out in an ATR-type optical set-up with extremely high throughput.

COLL 472 Branched poly(N-ispropyl acrylamide)s: Synthesis critical behavior and biological properties

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Poly(N-isopropyl acrylamide) (PNIPAM) is the most well-studied stimulus responsive polymer. Materials based on this polyerm have many uses in biotechnology including as smart surfaces for cell culture, as molecular components of sensors or in protein purification as well as in many other areas.

In this paper we will describe two types of branched PNIPAMs: a hydrogel brush system and highly branched polymers with functional end groups. Stimulus responsive hydrogel brushes are composed of a network of a permanently hydrophilic polymer, which is grafted with stimulus responsive chains. The networks display critical swelling behaviour, which is observed as step change in both the weight fraction of water in the system and the volume swelling, at approximately 32^{o}C. However, the contact angles change by only a few degrees at the critical point. The networks are useful as substrates for the cell culture of human condrocytes, which are cultured above the critical temperature and can be lifted from by lowering the temperature below the critical temperature. Other soluble branched PNIPAMs can be produced by copolymerizing NIPAM with a styrene monomer that is derivitised with a dithionate ester group. The latter group acts as a transfer agent in a RAFT polymerization of NIPAM. The resultant polymers have chain ends derived from the dithionate ester and have been used in thermally responsive protein purification strategies. The can prepared with imidazole, carboxylic acid or peptide end groups. The branched architecture has an effect on the lower critical solution temperature and influences the state of aggregation of the polymers below the critical solution temperature.

COLL 473 Molecular weight and density dependence of the temperature dependent collapse of grafted PNIPAM

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The temperature dependent collapse of poly(N-isopropyl acrylamide) is exploited in a wide variety of applications ranging from viscosity modification to tissue engineering. Although it is widely believed that the LCST is at 32C, there is evidence that the extent of collapse of grafted chains depends on the polymer architecture. Our findings show that the thermally induced changes in the PNIPAM chains depend on the molecular weight and grafting density. We quantified the interfacial forces, molecular thickness, and wettability of PNIPAM grafted from self assembled monolayers. Direct force measurements reveal a systematic decrease in the extent of chain collapse with decreasing density and molecular weight. At low densities, PNIPAM does not exhibit any change at the LCST, nor is there evidence for any shift in the transition temperature. These findings show that the design parameters for tuning the interfacial properties of PNIPAM films include both the chain architecture and the temperature.

COLL 474 Smart microfluidic channels from responsive polymer brushes

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We fabricated the walls of microfludic “smart channels” coated by responsive mixed polymer brushes with a gradient of chemical composition. The concept of the smart channels is based on switching/adaptive behavior of the mixed polymer brushes when wetting and non- wetting can be tuned upon interaction with liquids. This design of microfluidic channels brings new opportunities for manipulating the passage of liquids in the channels. The developed approach allowed us to fabricate three microfluidic elements for separation, sensing, selection and dosing microvolumes of liquids.

COLL 475 Controlled uptake and release of proteins by spherical polyelectrolyte brushes in aqueous solution

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In recent papers we showed that large amounts of proteins like bovine serum albumin (BSA) or ribonuclease A can be embedded in spherical polyelectrolyte brushes (SPB) by direct adsorption of the protein from solution [1-3]. The SPB consist of a solid polystyrene core of 100 nm diameter onto which linear polyelectrolyte chains like (poly(acrylic acid) or poly(styrene sulfonic acid)) are densely grafted. The adsorption of BSA and of other proteins was studied at various pH and at different concentrations of added salt. Surprisingly, we observe strong adsorption of BSA onto the SPB despite the effect that the particles as well as the dissolved BSA are charged negatively. The adsorption of BSA is strongest at low salt concentration and decreases drastically with increasing amounts of added salt. Virtually no adsorption takes place at salt concentrations over 0.1M. Here we discuss the controlled release of adsorbed proteins when raising the ionic strength again. We show by these experiments that the main driving force of the adsorption process is located in the release of numerous counterions of the brush. Moreover, we discuss possible applications of these nano-structured particles in biotechnology as e.g. for protein separation in solution or as carrier particles for enzymes. [1] A. Wittemann, B. Haupt, M. Ballauff, Phys. Chem. Chem. Phys. 2003, 5, 1671. [2] S. Rosenfeldt, A. Wittemann, M. Ballauff, E. Breininger, J. Bolze, N. Dingenouts, Phys. Rev. E 2004, 70, 061403. [3] Biomacromolecules 2005, 6, 948

COLL 476 Intelligent design: Bernasek and the evolution of analytical and surface chemistry

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For fifteen years, Steve Bernasek has provided vital leadership in the National Science Foundation's support of research in analytical and surface chemistry. First as a Visiting Scientist in the NSF's Chemistry Division in 1991-92 and for the subsequent fourteen years as an ‘Off-Site' Program Officer, Steve has very effectively used his vision, creative intellect, and interpersonal skills to guide the development of this then-new-to-the-Foundation program and to serve as a strong advocate and mentor for the surface chemistry community that is supported by NSF. His leadership has led to a surface chemistry research portfolio for the Foundation that is scientifically broad, intellectually strong, educationally rich, and characteristically diverse. This presentation will examine the evolution of the NSF Analytical and Surface Chemistry Program and highlight the impact of Steve Bernasek's intelligent design on that activity.

COLL 477 Surface chemistry on single crystal titania

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The rutile (110)surface continues to serve as a prototypical model system for surface science investigations of thermally and photon driven chemistry. Atomically resolved scanning tunneling microscopy results for tungsten trioxide, water and small alcohols on rutile (110)will be presented.

COLL 478 Surface chemical nature of Zn^{2+} in $Zn_xNi_{1-x}O$ solid solutions

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$Zn_xNi_{1-x}O$ solid solutions have been studied by X-ray diffraction (XRD) , Auger electron spectroscopy, (AES), X-ray photoelectron spectroscopy (XPS) and chemisorption, with supporting HF calculations. Both metals are formally M^{2+}, their stable oxidation state in the solid state, but the octahedral coordination of the $Zn_xNi_{1-x}O$ rocksalt structure is unusual for zinc which is typically tetrahedral, for example as is found in ZnO. In the bulk, $Zn_xNi_{1-x}O$ forms a solid solution over a concentration range of approximately $0 \leq x \leq 0.4$ and, although some zinc surface segregation is observed in these samples, the solid solution persists at the surface with the unusual chemical environment of the zinc cation shown by XPS Auger parameter analysis. The unique chemical environment of the zinc-nickel oxide solid solution results in new and interesting surface reactivity, and can potentially be used to tailor the metal oxide surface properties.

COLL 479 Using valence band photoelectron spectroscopy to identify subtle chemical differences

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Valence band X-ray photoelectron spectroscopy (XPS) gives spectral features (peak positions and peak intensities) that arise from different physical principles than the core spectral region. This difference leads to the valence band region providing complimentary information to that of the core region. In many cases the valence band region can be used to detect subtle chemical differences that cannot be determined in core XPS studies. The value of using valence band XPS interpreted by calculation models will be demonstrated for various systems, and the use of core and valence band XPS for the study of buried interfaces will be discussed. Examples discussed will include the formation and study of thin (less than 100ƒ≥) oxide-free phosphate films and the identification of different oxide films (including aluminum oxides) with similar chemical composition.

COLL 480 NiO(100) vicinally stepped surface adsorption of halobenzenes

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The adsorption of halobenzenes has been studied on vicinally stepped NiO(100) and the surface reactivity compared to that of the unstepped substrate by thermal desorption mass spectrometry (TDS), X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS). Bromobenzene, chlorobenzene, and iodobenzene were found to adsorb in two main states on the unstepped substrate: a molecularly adsorbed state and multilayer “ice”. The vicinally stepped substrate shows enhanced reactivity, forming a dissociative state at low exposures in coverages correlating with step density. The stepped substrate also shows a higher saturation coverage of the molecularly adsorbed monolayer at concentrations too high to be accommodated in a “ring-flat” adsorption geometry. HREELS analysis provides insight into the identity of this adsorbate and its bonding orientation and has been used in conjunction with Fourier deconvolution of the data to remove multiple phonon scattering effects from the HREEL spectrum.

COLL 481 Reactivity of anatase TiO2 nanoparticles: A comparative Density Functional Theory study of water, methanol and formic acid adsorption on the minority (001) surface

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Recent sum frequency generation work has shown that water, methanol and acetic acid are dissociatively adsorbed on colloidal anatase TiO_2 nanoparticles (NP) and the adsorption strength follows the order: acetic acid > methanol > water. Since calculations for the majority (101) surface of anatase NP cannot explain these results, we have carried out extensive density functional theory calculations of water, methanol and formic acid adsorption on the minority (001) surface, taking into account the effects of coverage, surface hydration and reconstruction. It is found that: (i) both clean and partially hydrated surfaces favor dissociation; and (ii) H_2O and CH_3OH dissociation is similar in energetics and kinetics, while HCOOH dissociation is easier and has higher adsorption energies. These results agree well with experiment, indicating that minority surfaces play a key role in NP reactivity.

COLL 482 Amphilic block copolymer self-assembly for directed synthesis of drug nanoparticles

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Nanoparticle formulations of drugs, printing inks, sun screens, and other hydrophobic organic compounds have distinct advantages in bioavailability, color intensity, and aesthetics. Common requirements of these applications are control of particle size and surface functionality. We present our new process --Flash NanoPrecipitation -- that produces stable nanoparticles at high concentrations using amphiphilic diblock copolymers to direct self-assembly. Uniform particles with tunable sizes from 50-500 nm can be prepared. The key to the process is the control of time scales for micromixing, polymer self-assembly, and particle nucleation and growth. The diffusion-limited assembly enables particles of complex composition to be formed. Examples of particle formation for controlled delivery of multiple drugs from nanoparticles will be presented, as well as formulations of nanoparticles in micro particles for aerosol drug delivery. A novel strategy for producing nanoparticles from soluble active compounds is demonstrated that enables the simultaneous encapsulation and controlled release of both hydrophobic and hydrophilic actives. The incorporation of gold nanoparticles and organic compounds into single nanoparticles enables simultaneous delivery and medical imaging. Finally, the ability to dry the nanoparticles by lyophilization or spray drying and to reconstitute them without aggregation greatly enhances the applicability of the technology.

COLL 483 Amphiphilic polymers for emulsion stabilization

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Amphiphilic polymers can be employed to stabilize emulsions without the use of low molar mass surfactants. In this contribution we report on two different approaches. In the first, a combination of two types of polymers was employed where one is interface active and the other thickens the continous phase of the water in oil emulsion. This allows for a separate control of droplet size and rheological properties. In the second approach temperature sensitive microgels based on poly-N-isopropylacrylamide (PNIPAM) are employed. Such microgels change their hydrophobicity with temperature and can stabilize emulsions similar to Pickering emulsions. We discuss the influence of microgel composition and oil polarity on the emulsion stability.

COLL 484 Fabrication of chemically and topologically heterogeneous patterns on the surface of amphiphilic block copolymers

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A novel fabrication of the chemically and topologically heterogeneous patterns on the surface of polymeric films over an area of more than 1 square centimeter in a single step was demonstrated by using the amphiphilic rod-coil type block copolymers such as polystyrene-b-oligothiophene block

copolymers and polystyrene-b-polyisoprene with polyhedral oligomeric silsesquioxanes-modified side chains. Hexagonally arranged open pores of a size of approximately 2 µm are spontaneously formed by casting the polymer solution under a moist air flow. The amphiphilic character of the rod-coil type block copolymers played the crucial role as a surfactant to stabilize the inverse emulsion of water droplets in the organic solvent. The characteristic imaging of transmission electron microscopy and time-of-flight secondary ion mass spectrometry clearly indicated that the hydrophilic rod segments form the aggregated structure on the interior of the open micropores on the surface while the flat area on the surface was covered with the polystyrene.

COLL 485 Nano- and micro-spheres with chemically patterned surfaces derived from amphiphilic diblock copolymers

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Different methods including emulsion polymerization have been used for the preparation of polymer nano- and micro-spheres with intricate internal domain structures. There have been, however, few reports on the preparation of polymer nano- and micro-spheres with segregated polymer chains on their surfaces. This talk will discuss how to use block copolymers in two ways to make nano- and micro-spheres with chemically patterned surfaces. One of these methods involved the use of two different amphiphilic diblocks as surfactants to aid the formation of oil-in-water emulsion droplets. By utilizing proper block copolymer and experimental design, we have been able to force the different diblocks to partition at the interface between water and each oil droplet. We then evaporated the oil and produced solid nano- and micro-spheres with chemically patterned surfaces. Even more interesting, the spheres could be produced to bear small surface hemispherical bumps where one type of surface chains resided predominantly.

COLL 486 Multiply-bound polymer chains of end-functionalized telechelics and block copolymers: A surface adsorption study by quartz crystal microbalance methods

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In this work, we present recent results on the modification of gold surfaces with alpha;omega;-functionalized telechelic polymers as a method for creating surfaces containing a high density of multiply bound polymer chains (MBPCs), i.e. “polymer loops”. Well-defined polymers with alpha;omega;-thiol functional groups were obtained via reversible addition fragmentation chain transfer (RAFT) polymerization and used as model compounds in this project. Adsorption of these polymers onto a gold substrate was studied in detail to systematically examine the effect of molecular weight and composition on the formation of MBPCs tethered to the surface. Quartz crystal microbalance with dissipation (QCM-D) was primarily employed to follow the in-situ adsorption and viscoelastic properties of the surface-bound telechelics. We will also report studies on a series of triblock copolymers of PVP-PS-PVP composition and their adsorption behavior.

COLL 487 Interfacial behavior and cross-linking at the air/water interface of amphiphilic star block copolymers based on polybutadiene and poly(ethylene oxide)

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Using purposely designed tri- and tetracarbanionic initiators, original amphiphilic Polybutadiene-b-Poly(ethylene oxide) star block copolymers ((PB-b-PEO)n = 3 or 4) of well-defined molar mass,

composition and architecture could be obtained by sequential anionic polymerization of butadiene and ethylene oxide. Isotherm experiments at the air/water interface showed the following three characteristic regions : a compact brush region, a pseudoplateau at a pressure of ca 10 mN/m, and a pancake region where the observed surface area depended on the amount of PEO present. The elasticity properties of the monolayer were examined by repetative compression/expansion cycles and resulted in reproducible hysteresis at different pressures. The monolayers were also transferred as Langmuir-Blodgett films on mica at various surface pressures and analyzed by Atomic Force Microscopy (AFM), demonstrating different morphologies from analogous (PS-b-PEO)4 star copolymers. The monolayers were subsquently cross-linked at the air/water interface in the presence of AIBN and UV irradiation.

COLL 488 New chitosan hydrogels: Mechanical properties and multiscale microstructure

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The structure of the solutions and gels of chitosan are studied by X-ray and light scattering techniques (SAXS, WAXS, SALS, WALS). The structure of chitosan solutions is displaying the polyelectrolyte peak and a low angle upturn related with chain aggregation. The detailed study of this morphology enables to characterize chitosan as a solvophobic polymer in water and propanediol/water mixtures in the contect of the pearl-necklace model. Gelation is obtained by neutralization or by increasing the solvobicity of the polymer. The nanostructure of the gels is also complex and was characterized from the micron range up to the interatomic distances. The nanostructure of the gels was followed by SAXS in situ during a compression test, in order to understand the dissipative visco-plastic behaviour of these multiscaled materials.

COLL 489 New functional carboxylic polymers for detergents

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It is well known that carboxylic polymers like polyacrylates and acrylate/maleate copolymers are generally used as a dispersant and chelant in global laundry detergents area. New functional carboxylic polymers, such as a polyacrylate with narrower molecular weight distribution (Mw/Mn) and an acrylate/maleate copolymer with well-regulated monomer unit sequences, have been manufactured by precisely controlled polymerization process. Meanwhile, polyethylene glycol grafted carboxylic polymer, polyacrylate with chelating sites (iminodiacetate etc.) and polyethylene imine based zwitterionic polymer have also been prepared to install additional performance. These carboxylic polymers gain stronger or additional interaction with surfactants and/or hydrophilic and hydrophobic stains. And these polymers have outstanding performances, which are clay dispersion ability, anti-soil redeposition on fabrics and prevention of heavy metal (Fe etc.) issue in cleaning.

COLL 490 Inorganic, metal and semiconductor nanoparticles stabilized by acetal-PEG/polycation block copolymers: Bionanoparticles for new diagnostics, bioimagings and therapeutics

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Acetal-ended poly(ethylene glycol)-b-polycation block copolymers (acetal-PEG/polycation) were prepared by our original synthetic route. When the acetal-PEG/polycation block copolymers were mixed with several nanoparticles such as inorganic, metal and semiconductor nanoparticles, the polycation segment in the block copolymers adsorbed on the particle surface to stabilize them under the physiological conditions because that the PEG segment in the block copolymer locates on the particle surface to form tethered chain fashion. The acetal group locates at the end of the PEG chain can be converted to aldehyde group by the acid treatment, followed by the installation of a ligand molecule via a suitable conjugation reaction. For example, an aminophenyl lactose can be conjugated at the CHO-PEG chain end via a reductive amination reaction by sodium borohydride. Such particles are promising as a tool for biofunctionalized materials not only for nano-diagnostics but also for bioimaging, nanomedicine and nanocarriers for drug delivery systems.

COLL 491 Mechanisms responsible for the tribological properties of PTFE transfer films

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Mechanical devices for space applications need to be able to operate reliably in an extreme range of environments. Therefore, the physical and chemical integrity of the materials has to be assured under extremes of both high and low temperature, under ambient pressures and in near absolute vacuum, and under solar radiation. Polytetrafluoroethylene (PTFE) is known for its low frictional coefficient and good thermal and chemical stability. For this reason, polymer nanocomposites based on PTFE are being considered for use as solid lubricants in aerospace applications. Not surprisingly, many properties of PTFE depend on its local morphology. In this study, classical molecular dynamics (MD) simulations are performed to examine the effect of surface chain configuration on the frictional behavior of PTFE at the molecular level. The goal is to identify the fundamental wear mechanisms and to guide the refinement of new, PTFE-based composite materials. The results indicate that local chain structure and debris molecules at the sliding interface have profound effects on the tribological properties of PTFE transfer films. These findings are in excellent agreement with experimental results.

COLL 492 Molecular sensors: Measuring friction coefficient between fluid monolayers and solid substrate

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Flow properties of molecularly thin films are at the heart of many practical applications such as coatings, microfluidics, and lubrication. In fluid monolayers however, how do we assess the driving and frictional forces that are intimately related to the molecular interactions between the fluid and the solid surface? In this regard, visualization of flowing molecules demonstrates an exceptional ability, in particular when the molecules are compressible. Here we report on monitoring of pressure-responsive macromolecules as they drastically change shape in response to variations in the film pressure present within the flowing monolayers. After appropriate calibration, these molecular sensors provide independent measures of both the pressure gradient and the friction coefficient of spreading polymer films. The friction coefficient revealed strong dependence on relative humidity of the surrounding atmosphere.

COLL 493 Temperature dependence of microscopic friction measurements

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The temperature dependence of interfacial friction measurements performed in the temperature range of 100-300 K under ultrahigh vacuum environments for a range of materials contacts will be described. These measurements have been conducted with atomic force microscopy with the intent of assessing sliding in the regime of wearless friction. In particular, the results obtained for the

contact of a silicon nitride tip with a graphite surface will be presented in terms of an activated sliding mechanism that can be described in terms of an Arrhenius model.

COLL 494 Heat transfer at the interface of model diamond {111} nanosurfaces

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Heat transfer from a small, hot diamond {111} nanosurface brought into contact with an identical larger, cold nanosurface was studied using classical molecular dynamics method. Kinetics of the energy transfer across the nanosurfaces' interface was found to be exponential with a rate constant depending on the force applied to the hot surface, its thickness, and the chemical and isotopic composition of the interface. The rate constant of the heat transfer did not demonstrate significant changes with the increase of the temperature gradient between the nanosurfaces and the increase of the surfaces' contact area.

COLL 495 Tribological investigations of a low friction, low wear polymer/polymer composite

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Wear resistant and low friction solid lubricants offer the design engineer attractive options for extreme environment lubrication, particularly in situations where the use of fluid lubricants are precluded. The tribological properties of composite samples ranging from 0-100 weight percent PEEK filled PTFE were evaluated in this study. A linear reciprocating tribometer was used to evaluate the tribological performance of this material on lapped AISI 304 stainless steel counterfaces with an average roughness of 161 nm Rq. Test conditions include a nominal contact pressure of 6.2 MPa, a reciprocation length of 25.4 mm and a sliding speed of 50.8 mm/s. In general, the composite samples had lower coefficients of friction than unfilled PTFE and PEEK, which had friction coefficients of $\mu=0.135$ and $\mu=0.363$ respectively. Friction coefficient appears minimum at approximately 50 wt% PEEK with $\mu=0.111$.

COLL 496 DPD Simulation of conformation and behavior of end-grafted Diblock Copolymer under compression and shear

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Dissipative Particle Dynamics was used to investigate the friction behavior and conformation of diblock charged copolymers (PtBMA-b-PSGMA) end-grafted at hydrophobic surfaces in aqueous media for different copolymer molecular weights, degrees of ionization, grafting densities, surface separations between two opposing surfaces and as one of the surfaces was made to slide past the other one at different separation distances. The simulation data agree very well with previous experimental results as well as with observations for other theoretical approaches. Highly charged chains have shown to not interpenetrate upon compression between two opposing surfaces for small contact areas, whereas for large contact areas, some opposing chains exhibit a slight degree of interpenetration. The interpenetration thickness has shown to be dependant on the degree of ionization of the chains and friction coefficient between two opposing polymer-coated surfaces has shown to be directly correlated with the extent of interpenetration layer thickness.

COLL 497 Friction behavior of aligned multi-walled carbon nanotubes

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This presentation will highlight results on the tribological behavior of aligned multi-walled carbon nanotube films and composites derived from them. MWNT films showed highly anisotropic tribological behavior for films oriented in mutually orthogonal directions. The average values of coefficient of friction varied by an order of magnitude from 0.795 for vertically aligned nanotubes grown on rigid substrates to .090 for nanotubes dispersed in the plane of the same substrate. Due to the closed shell nature of the MWNT, the coefficient of friction was insensitive to humidity. It was found that the order of magnitude difference in the coefficient of friction was due to an order of magnitude difference in contact area between the vertically and transversely aligned tubes. A strong temperature dependence was observed and could be controlled by altering the counterface surface chemistry. Composite studies are ongoing and will be a second focus of this talk.

COLL 498 Rheology of sub-nanometer thick water films

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Knowing the behavior of water in small volumes is essential for the understanding of many processes in biology, tribology, and geophysics. Water under nano-confinement plays a crucial role in biological and technological systems. Here, we report an experiment in which an atomic force microscope tip approaches a flat solid surface in purified water, while small lateral oscillations are applied to the tip. The normal and lateral forces acting on the tip are measured directly and simultaneously as a function of water thickness. We find that, for hydrophilic surfaces, oscillatory solvation forces are present in the last four adjacent water layers where the dynamic viscosity is measured to grow up orders of magnitude in respect to bulk water. The same effects are present for atomically smooth surfaces and slightly rough surfaces. Oscillatory solvation forces have been detected also when the confining flat surface was hydrophobic.

COLL 499 A first principles approach to simulating electrocatalysis

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Electrocatalysis is controlled by the elementary reactions that occur at the interface between the electrode and the solution phase and requires an accurate accounting of the electrochemical potential that results across this interface. Elucidating the electrochemical behavior at this interface, however, presents a considerable challenge due to complexity of the surface chemistry, the explicit atomic and molecular structure of the solution phase at the interface, the presence and formation different ions, and the applied surface potentials that result as a function of the surface reactivity. First principles modeling of electrocatalysis also tends to be limited by the fact that ab initio methods simulate constant charge systems rather than constant potential systems. We have developed an approach by which we can begin to approximate the simulation of constant potential systems. The approach is used herein to model both the oxidation methanol and the reduction oxygen. More specifically, we follow the potential dependent behavior for methanol decomposition and oxidation, the electrocatalytic reduction of O2 reaction paths and in addition the competing adsorption from the electrolyte.

COLL 500 Role of liquid products in catalyst pores for influencing product olefin readsorption and hydrocarbon chain initiation in Fischer-Tropsch synthesis

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During Fischer-Tropsch synthesis, catalyst pores are filled with waxy liquid product hydrocarbons. In the absence of H_2 and CO fugacity gradients, this liquid phase helps to increase the overall reaction rates for the readsorption of product α-olefins which in turn increase hydrocarbon chain initiation. This results in non-linear Flory product distribution and the formation of a heavier more paraffinic product slate. We use transition state theory to show that higher olefin readsorption rates of larger olefins are not the result of higher solubility of olefins in the liquid phase. Increasing olefin solubility is either unimportant for olefin readsorption, or, under certain circumstances, would actually increase the tendency of adsorbed olefins to desorb rather than of solvated olefins to readsorb. Thus the olefin solubility – physisorption model is inconsistent with transition state theory and with experimental observations. Instead, the liquid hydrocarbon phase within catalyst pores introduces an intraparticle transport limitation on the olefin products as they exit these pores. These intraparticle diffusion limitations induce fugacity gradients that lead to the observed enhanced olefin adsorption as olefin size increases within catalyst pores. Indeed, this is further substantiated when product selectivity is plotted versus critical catalyst physical parameters that define the Thiele modulus. If, however, these parameters are altered so that the hydrocarbon liquid phase within the catalyst engenders the formation of CO and H_2 gradients within the pores, selectivity to heavy hydrocarbons is reversed and lighter products are made. Thus the liquid product can affect various fugacity gradients within Fischer-Tropsch catalyst pores, consequently determining the hydrocarbon distribution during synthesis.

COLL 501 Statistically-designed study of FTS reaction kinetics on Fe

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Fischer-Tropsch synthesis kinetics on Fe catalysts has been well studied; indeed, more than a dozen papers report reaction rate expressions and kinetic parameters [1]. However, in several previous studies, experimental conditions and catalyst properties were chosen without adequate regard to effects on reaction rate of heat/mass transport disguises and catalyst deactivation [1].

It is surprising that none of the previous kinetic studies FTS on Fe incorporated a rigorous statistical experimental design while few studies used accepted statistical methods to regress and evaluate the significance of their fitted parameters. Since design of experiment (DOE) methods are readily available in the literature and have been shown to enable (1) reduction of the number of experiments, (2) determination of fitted parameters with much greater accuracy, and (3) evaluation of interactions between variables, it is a wonder they are not being used.

We will present the results of a statistically-designed set of experiments, involving sequential DOE, to determine reaction kinetics of FTS on a $FePt/La_2O_3$-Al_2O_3 catalyst. This catalyst was coated on a ceramic, cordierite, cellular monolith (Celcor—Corning Inc.) to facilitate collection of rate data in the absence of pore-diffusional restrictions; it was designed to be stable over weeks of operation. Data were collected in a gradientless, stirred-gas recycle Berty reactor to minimize effects of heat and mass transport at conditions representative of commercial operation. Rates of hydrocarbon production were fitted by nonlinear regression to various shifting-order rate expressions (e.g. Langmuir-Hinshelwood) derived from a widely accepted sequence of elementary steps. The results of the nonlinear regression of the data and the statistical evaluation of the data and fitted parameters will be presented in some detail.

References

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COLL 502 Catalysis in a nanocage environment

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It has long been recognized that the environment around an active site influences the catalytic behavior. A reaction catalyzed by an active site in a zeolites cavity may be influenced by the window size that control access to the cavity, and by partitioning effect due to preferential adsorption of one molecule to another. However, there are few examples of cage effect in inorganic catalysts outside zeolites, although it can be found readily in biological systems (enzymes). Here we present our investigation of the properties of amine active sites in a 2 nm size siloxane nanocage. The shell of the cage provides molecular size selectivity, and the cage environment demonstrates concentration effect. The preparation and characterization of the cage will be presented.

COLL 503 Synthesis and characterization of supported metal catalysts derived from metal-dendrimer nanocomposites

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We have been investigating the utilization of dendrimer-metal nanocomposites for the preparation of heterogeneous supported metal catalysts with controlled particle sizes. Poly(amido)amine (PAMAM) dendrimers contain amine and amide groups arranged in regular patterns, which have the ability to complex metal cations into their branches. Commercially available PAMAM dendrimers were used to prepare dendrimer-metal nanocomposites in solution, incorporating different noble metals (i.e., Pt, Ru, Rh). The complexation and subsequent reduction processes were monitored in-situ via the use of UV-Vis and EXAFS spectroscopies. The metal-dendrimer nanocomposites were then supported onto metal oxide supports via incipient wetness impregnation and/or adsorption processes. The resulting materials were thermally treated under various oxidative and reductive protocols to remove the dendrimer component and obtain supported metal catalysts. These processes were once again, monitored in situ via EXAFS and FTIR spectroscopies. Finally, the resulting catalysts were examined for a number of catalytic reactions including the oxidation of CO in the presence and absence of hydrogen, the hydrogenation of propylene and the hydrogenolysis of ethane. The results of the characterization efforts document the substantial changes taking place in the nature and environment of the metal species involved (i.e., oxidation state and coordination number) during the synthetic process, as well as changes in the dendrimer's functional groups during metal complexation and dendrimer decomposition/desorption. The presence and type of incorporated metal, as well as the nature of support used, further influences the pathway and rate of these processes. The results also demonstrate that depending on the nature of the metal, the use of dendrimer-metal nanocomposites can lead to the synthesis of unique catalytic materials with a narrow distribution of metal particle sizes and different catalytic properties than conventionally-prepared supported metal catalysts.

COLL 504 Heterogenization of homogeneous metal complex catalysts degrades catalytic properties: Confronting the dogma

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Dogma in the catalysis field states that immobilization of homogeneous metal complex catalysts generally leads to poor catalytic properties relative to the free molecular catalyst. In this work, we discuss how knowledge of reaction mechanism can guide the choice of what homogeneous metal complex catalysts might be supported in a manner where good catalytic properties are maintained. Two specific cases will be considered, (a) discrete Pd(0) or Pd(II) metal complexes for C-C bond forming reactions such as Heck or Suzuki couplings, and (b) Co(III) salen complexes for the hydrolytic kinetic resolution (HKR) of racemic epoxides. New experimental results on the use Pd(II) PCP and SCS pincer complexes in Heck reactions, coupled with a detailed analysis of the reaction mechanism along with the current and historic literature lead to the hypothesis that immobilization of such discrete metal complexes for use as recoverable, recycleable Heck catalysts may not be feasible. In contrast, knowledge of the reaction mechanism in Co(III) salen catalyzed HKR can be used to guide the proper design of supported catalysts, with optimal designs leading to supported catalysts with substantially increased rates and comparable ee's (>99%) compared to the original homogeneous analogue.

COLL 505 Dielectrophoretic assembly of bionanocomposite materials from live cells and functionalized particles

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We have previously shown that dielectrophoresis can be used for making a range of assemblies from nano- and microparticles. In this study we extend the method of controlled on-chip dielectrophoretic assembly to making of permanent structures from live cells. Alternating electric fields were applied across suspensions of cells, such as baker's yeast and NIH/3T3 mouse fibroblasts, to assemble 1-D chains and 2-D arrays. The cells were further combined with synthetic nano- and microparticles that bound the cells via biospecific key-and-lock interactions. The use of magnetic particles imparted an additional functionality to the live cell matrix and we were able to manipulate the materials using an external magnetic field. The new biocomposites include cell “wires” that can be components of bioelectronic circuitry or 2D cell membranes that can be applied in sensors, coatings, bioreactors and biomedical implants. Thus, we demonstrate a simple novel technique to synthesize “smart” multifunctional bio-composite materials.

COLL 506 Magnetic fluid mediated manipulation and orientation of colloidal components

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Compared with optical tweezing and dielectrophoresis, magnetic field manipulation techniques have fundamental advantages uniquely suited for arranging micro- and nano-scale components in fluids. In comparison with past work, which has focused primarily on manipulating magnetic particles immersed in a non-magnetic solvent, herein a novel method is presented for manipulating non-magnetic colloidal particles immersed in a ferrofluid (a fluid densely concentrated with <10 nm diameter magnetic nanoparticles). The advantage to the proposed technique is that it facilitates the manipulation and orientation of biological materials, such as viruses, bacteria, large proteins and polymers, as well as host of inorganic materials, such as metallic and semiconducting nanoparticles, without requiring direct attachment of the materials to a magnetic particle carrier. This talk will focus on theoretical and experimental results from the ferrofluid immersion approach in applications ranging from stretching molecules to assembling gold nanoparticle arrays on a substrate.

COLL 507 Gold nanoparticle templated synthesis of *p*NIPAm nanogels

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The synthesis of small hollow polymeric nanoparticles for drug delivery and enzyme encapsulation is an expanding area of research. Previous methods towards the production of sub-50 nm polymer particles have utilized cross-linking of polymer micelle surfaces, metathesis polymerization of covalently bound monomer monolayers and layer-by-layer adsorption of polyelectrolytes on spherical nanoparticles. However, an in-situ free-radical polymerization method for producing sub-50 nm hollow hydrogel nanoparticles is still to be developed. In the current work, we have explored a synthetic route towards poly (N-isopropylacrylamide) (*p*NIPAm) nanogels by growing a *p*NIPAm shell on metal nanoparticle seeds. Nuclei compatible with precipitation polymerization of thermoresponsive polymers can be formed by adsorption of NH_2-terminated *p*NIPAm on ~13 nm gold nanoparticles. When heated to 70 °C (above the LCST of *p*NIPAm) the adsorbed *p*NIPAm layer collapses onto the gold nanoparticle surface. This polymer layer serves as a hydrophobic nucleus for growing *p*NIPAm oligoradicals during the synthesis, resulting in the formation of a *p*NIPAm shell. Etching of the gold core from the polymer coated particles with KCN addition results in hollow hydrogel nanoparticles. Future studies are aimed at understanding the encapsulation of small molecules and proteins within the nanocapsule structure.

COLL 508 Evaporative deposition of bacteria on surfaces: Two dimensional films, cellular patterns and potential for constructing living functional materials

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Bacterial cells are in essence self-contained, highly complex, nanoscale machines. With recent advances in synthetic biology there is enormous potential to use the combination of biology and nanotechnology to build living nanostructures with new functionalities. In nanotechnology, device construction involves spatial and temporal manipulation of the component building blocks. While single cells can be manipulated, this process becomes prohibitive for a large number of cells. Little is known about how to control deposition of bacteria on surfaces. Controlled deposition would allow incorporation of the cell-cell communication capabilities uniquely available to living bacteria in the device design. We have used evaporation directed assembly to produce viable two-dimensional bacterial films with intriguing networked spatial patterns (cellular films) and have developed a method to measure the elastic and adhesive properties of these films using a surface force apparatus.

COLL 509 Bio-inspired, kinetically controlled low-temperature catalytic nanofabrication of template-free metal hydroxide, phosphate and oxide thin films

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We discovered the mechanism governing biological nanofabrication of silica and translated this mechanism to develop a new low-temperature, kinetically controlled catalytic route for synthesis of a wide range of nanostructured metal hydroxide, phosphate and oxide thin films without using organic templates. Many of these materials could not be made in thin film morphologies by conventional

high-temperature methods. Because no organics or templates are used, the electronic properties of the resulting materials can be measured free of influence from those sources. As proof of principle, we used this process for the low-temperature synthesis of photovoltaically active thin films of cobalt hydroxide. These exhibit high dopant density, high surface area single-crystal domains, exceptionally long minority carrier lifetime and strong absorption in the visible. Because no organics are used, this new biologically inspired synthesis method yields exceptionally pure inorganic semiconductors, and thus is potentially integrable with conventional manufacturing methods.

COLL 510 Growth of biomolecular mesoporous microcrystals

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Protein and virus crystals offer some unique properties in that they are mesoporous materials (2 - 20 nm) that consist of chemically heterogeneous pore walls. These pores are tunable in size depending on the crystal structure and occupy 30-70% of the total crystal volume. These crystals are useful for a variety of applications such as catalysts, stationary phases for chromatography, or adsorbents for toxic metals in waste water. However the performance of these applications could be enhanced by using smaller crystals which will allow greater mass transport within the crystalline material. Here we discuss methods for controlling biomolecular crystal growth to achieve uniform sub-micron crystals and we will highlight the crystals potential use as a toxic metal adsorbent.

COLL 511 Preparation of tin oxide-germania hybrids via biomineralization

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Nanocrystalline tinoxides were grown by biomineralization in the presence of amino acids such as lysine, arginine and histidine. The effect of the size and the shape of the nanocrystals formed was studied using different precursors of tin oxides. Hybrids of tin oxides with germania were also prepared in the presence of the above amino acids. The growth was monitored over a period of time at varying pH. It was observed that the yields were higher at pH 6 – 8. At very high pH (greater than pH 12), however agglomeration was observed and amorphous aggregates were obtained. The samples obtained were found to be nanoporous. The utility of the tinoxide materials as a sensor for NO2 gas is being studied. In addition, since germaninum dioxides have reduced phonon energies compared to their silica counterparts, such hybrid materials can also be used for fabrication of new optoelectronic devices.

COLL 512 Particle into liquid sampler (PILS) for Southern California PM-2.5 analysis

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Air pollution in the Southern California Air Basin migrates daily from the coast to the inland areas. As air parcels move across this highly developed region, gas phase and aerosol pollutants accumulate. Fine particulates (PM-2.5) are formed by a variety of chemical reactions during this migration. A Particle Into Liquid Sampler (PILS) coupled to ion chromatographs is used to characterize the ion chemistry of the PM-2.5, including ammonium, potassium, sulfate, nitrate, etc in Claremont, California. These measurements are taken on short time scales to identify trends in ion chemistry, such as the diurnal cycles of ammonium and nitrate observed during previous sampling cycles. Charge balance between the ions can also provide insight into ion chemistry in pollution plumes. A

Tapered Elemental Oscillating Microbalance (TEOM) is used to measure total PM-2.5 mass while an onsite weather station is utilized to correlate PM chemistry with temperature, wind speed and direction, and humidity.

COLL 513 Heterogeneous reactions on ice

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Ice and snow are common materials in the environment and reactions over ice surfaces have significant impact to the atmosphere. Aimed to understand atmospheric S(IV) oxidation processes near ice/snow surfaces, we have studied SO_2 uptake on HOX-treated ice surfaces. The study has been carried out in a flow reactor at 190-240 K. Uptake coefficients were determined as a function of surface coverage, temperature, and ice film thickness. Kinetic results are discussed in terms of the Eley-Rideal mechanism. This study suggests that the uptake of SO_2 is enhanced by the presence of HOBr or HOCl molecules near the ice surface.

COLL 514 Surface thermal reactivity and photochemistry of HNO_x in a supported aqueous phase

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The thermal and photochemical transformations of HNO_3 to HNO_2 in water and ionic solutions supported on heterogeneous media were examined under environmentally relevant experimental conditions. Complementary kinetics simulations, molecular dynamics studies, and density functional calculations were carried out. The observed kinetic profiles are examined in terms of differential dynamics of solvated and adsorbed species within and between the microenvironments of the supported aqueous phase. The observed photochemical activity spectrum is interpreted in the context of proposed reactive pathways.

COLL 515 Reaction dynamics of HCl and O_3 in collisions with ω-functionalized self-assembled monolayers

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The objectives of this work are aimed at elucidating the atomic-scale mechanisms of interfacial bonding, diffusion, and reactions that govern gas-surface interactions on model organic materials. This presentation will focus on recent molecular beam scattering studies of HCl and O_3 collisions with self-assembled monolayers (SAMs). The gases represent two important atmospheric species and the SAMs are chosen to mimic the surface of surfactant-covered organic aerosols that are also prevalent in the environment. These studies reveal how the atomic-scale nature of organic surfaces determine the extent of energy transfer, thermal accommodation, and subsequent reaction pathways for the gas-surface collisions. The experiments involving HCl impinging on OH-terminated SAMs have revealed that HCl can form 24 kJ/mol hydrogen-bonds with the monolayer, but the interaction is not significant enough to result in proton-transfer reactions. In the case of O3 colliding with an olefin-terminated SAM, reactions produce carboxylic-acid anhydride groups that crosslink adjacent SAM chains.

COLL 516 Surface reactions of gas phase radicals with polymers and self assembled monolayers

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The better understand the surface reactions of gas phase radicals with organic surfaces we have studied the interaction of atomic radicals with selected polymers and SAMs, the later used as models for polymeric interfaces. Atomic oxygen (AO) and atomic hydrogen (AH) both etch hydrocarbon polymers and alkanethiolate SAMs by forming a modified surface region, although the thickness of this nanometer scaled interface was significantly greater during AH exposure, due to the greater penetration depth of AH compared to AO. The site selectivity of radical-surface reactions is illustrated by the reactivity of AO and AH with semifluorinated SAMs (CF-SAMs). Reactions of AO with CF-SAMs are initiated exclusively at the film-substrate interface, leading to desorption of intact adsorbate chains. In contrast, AH permeates through the fluorinated segment of the CF-SAM, cleaving C-C bonds at the fluorocarbon-hydrocarbon interface; these differences have been rationalized on the basis of the reactivity of AH and AO.

COLL 517 Investigation of alkanethiol monolayers on reactive metal surfaces studied with sum frequency generation and electrochemistry

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An n-alkanethiol, octadecanethiol (ODT), monolayer was successfully prepared onto oxide-free mild steel (MS) surface under cathodic polarization in a 0.1 M LiCl/CH3OH solution containing 1 mM ODT. Cyclic voltammetry (CV), electrochemical impedance (EIS) and sum frequency generation (SFG) spectroscopy were applied to study and characterize the adsorption of ODT at a MS surface. In 0.1 M LiCl/CH3OH solution containing 1 mM ODT, CV of the MS electrode shows a dramatic decrease in charging current and a positive shift in oxidation potential when compared to a solution without ODT. The interfacial capacitance was obtained as 2.52 microF/cm2 from the impedance data. An average chain tilt angle of 48 degrees for the ODT molecules was deduced from the comparison of the interfacial capacitances of the ODT/MS and ODT/Au monolayers. X-ray photoelectron spectroscopy confirmed the formation of the ODT monolayer on mild steel. The ppp SFG spectrum of the ODT modified MS features three strong methyl vibrational modes at 2877, 2943 and 2967 cm-1, indicating the formation of the oriented and densely packed ODT monolayer. However, the appearance of the two weak CH2 groups vibrational modes at 2850 and 2914 cm-1 implies the presence of defects in ODT monolayer. ODT/Au films were prepared to compare with the ODT/MS films. Orientation analysis of the air/solid interface suggest that the methyl group of ODT/Au films have a tilt angle of 30 degrees, while the methyl group of ODT/MS films have a tilt angle of 23 degrees. Water was found to have an impact on the shape of the SFG spectra of ODT/MS. It suggests that solution penetrated through the defects to reach mild steel surface.

COLL 518 Complexity in the self-assembly of bi-functional molecules on HOPG: The influence of solvent functionality on self-assembled structures

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Self-assembled monolayers of bi-functional molecules HOOC(CH2)nCOOH, HOOC(CH2)nCH2OH and HOCH2(CH2)14CH2OH were investigated using scanning tunneling microscopy for understanding the functionality-induced self-assembly and the influence of acid solvent on molecular self-assembly. For di-acids, only HOOC(CH2)20COOH forms coadsorption structures with the solvent. The remaining di-acids form single component monolayers without coadsorption. This result suggests that the coadsorption with acid solvent occurs to maximize hydrogen-bond density in the overlayer. For HOOC(CH2)nCH2OH, the coadsorption of HOOC(CH2)14CH2OH and octanoic acid produces a microscopic mesh made of homogeneously arranged nanoscale openings. For HOOC(CH2)13CH2OH, however hydroxyl groups of two adjacent lamellae assemble to form a herringbone geometry and the two carboxylic acid groups assemble with a straight head-to-head configuration. The bi-functional

molecule HOCH2(CH2)14CH2OH exhibits multiple packing patterns on HOPG via different hydrogen-bonding networks. This investigation demonstrates the complexity of self-assembled structures formed from bi-functional molecules and the significant impact of solvent molecules on the formation of self-assembled monolayer.

COLL 519 Designing functional macrosurfactants via triblock tercopolymers

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The diverse methods of controlled free radical poymerization have not only opened an additional pathway to block copolymers, but have enlarged the pool of useful monomers for such polymers enormously. In particular for hydrophilic monomers, radical polymerization is much more tolerant than the other established methods, and thus enables the use of hitherto unpracticable building blocks. We are exploiting these opportunities to prepare novel triblock tercopolymers with functional hydrophilic and/or hydrophobic blocks, in order to induce complex self-organization effects. This comprises for instance internal nanostructuration of micelles and vesicles, or multiple stimuli-sensitive associative systems. Synthetic strategies and typical problems encountered are discussed, and the rich micellar self-organization of the functional tercopolymers is presented, with emphasis on the use of acrylic monomers.

COLL 520 Stimuli-responsive block copolymers via RAFT for applications in aqueous media

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Reversible addition-fragmentation chain transfer (RAFT) polymerization has been the focus of intensive research over the past few years since this methodology allows polymers with complex molecular architectures to be prepared with predetermined molecular weights and narrow molecular weight distributions. Using the RAFT process, we have synthesized a wide range of functional, water-soluble block copolymers. Stimuli-responsive polymers such as poly(N-isopropylacrylamide) (polyNIPAM) have been employed to prepare shell cross-linked micelles with potential applications as drug delivery agents while other non-immunogenic block copolymers such as poly(N-(2-hydroxypropyl)methacrylamide)-b-(N-[3-(Dimethylamino)propyl]methacrylamide) have been investigated because of their enormous potential as gene delivery agents. Synthetic methods leading to controlled architectures will be discussed as well as studies involving micelle formation and sequestration.

COLL 521 Enzymatic synthesis and characterization of hydrophobized poly (L-lysine)-amylose conjugates

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Amylose, a linear polysaccharide consisting of a-1, 4 linked glucose units, is an interesting macromolecule that complexes various hydrophobic guest molecules in the helical cavity in water. Amylose derivatives can be obtained from enzymatic polymerization by phosphorylase with maltopentaose derivatives as primers. We reported that methoxy poly(ethylene oxide)-block-amylose (MPEO-amylose) is a novel amphiphilic polymer having the amylose chain as a molecular recognition site (Akiyoshi, K. et al., Biomacromolecules 2002, 3, 280). In this study, hydrophobized poly (L-lysine) grafted maltopentaoses (CH-MaPLL) were synthesized as amylose-primers. The partial modification of maltopentaose-poly (L-lysine) (MaPLL) by hydrophobic cholesteryl groups leads to the formation of hydrogel nanoparticles (nanogels) by their self-associations (about CHPLL: Akiyoshi, K. et al., Macromolecules 2000, 33, 6752). CH-MaPLL copolymers were enzymatically polymerized in the presence of phosphorylase and glucose-1-phosphate. The degree of polymerization (DP) was linearly increased in accordance to the polymerization time. Characterization and function of CH-Amylose-PLL were reported.

COLL 522 Azobenzene-modified polymers forming light-triggered complexes with surfactants and amphiphilic colloids

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The challenges toward the development of light-responsive colloids carriers for controlled release produced a variety of polymers designed to reversibly self-assemble or fold upon exposure to light. Macromolecules containing photochrome monomers achieve this goal, though with a significant fraction of photochrome groups along their chains. We propose a new route that amplifies the molecular properties of photochrome by using colloid-polymer “recognition” and cooperative hydrophobic binding. We synthesized azobenzene-modified polyacrylate (HMP) with low density of photochromes (<3mol%). In aqueous solutions, HMP can bind to colloids such as surfactant micelles, lipid vesicles, and proteins. Macromolecules with optimal structure bind tightly to colloids in the dark, or under blue light, while almost complete dissociation can be observed under exposure to UV. Binding isotherms and composition of the complexes will be discussed with the aim of rationalizing the effects of HMP structure. Applications to light-triggered emulsifiers and to lipid membrane permeabilisation will be exemplified.

COLL 523 Cross-linked amphiphilic block copolymers: Synthesis, characterization and modeling

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Hydrophilic and hydrophobic monomers have been combined by group transfer polymerization (GTP) to produce amphiphilic conetworks of controlled structure (model conetworks) of three different types: (a) regular model conetworks, in which all polymer chains are linked at their ends, leaving, in principle, no free chain ends, (b) cross-linked star polymer model conetworks, in which star polymers are interlinked via half of their chains, letting the other half free (dangling), and (c) shell-cross-linked polymer model conetworks, in which the outer body of the network is decorated by polymeric arms (dangling chains). The amphiphilic character of these materials leads to microphase separation in water, which is investigated by swelling measurements, small-angle neutron scattering (SANS) experiments, and thermodynamic calculations. Unique features of the conetworks incorporated in these calculations are the existence of both bridges and loops in the continuous microphase and the presence of both stretched and compressed chains in the dispersed microphase.

COLL 524 Stimuli-responsive polymers with various shapes by living cationic polymerization

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Stimuli-responsive polymers of vinyl ethers with various shapes were synthesized via living cationic polymerization with a Lewis acid in the presence of an added base. (i) **Homopolymers.** Poly(vinyl ether)s with oxyethylene or alcohol pendants exhibited highly sensitive and reversible LCST-type phase separation in water. Photo- and pH-responsiveness with high sensitivity was also induced using polymers with azo and carboxy moieties, respectively. (ii) **Block Copolymers.** Reversible stimuli-responsive micellization and physical gelation were achieved using diblock copolymers of a stimuli-responsive and an "always-soluble" segment. Triblock copolymers with two different thermosensitive segments underwent unique physical gelation with two-stage transition. (iii) **Star-Shaped Polymers.** Thermosensitive star polymers with certain sequence distribution induced physical gelation in water on cooling, although their segments show LCST-type phase separation. Star polymers with thermosensitive parts in the arm or the core realized reversible encapsulation of hydrophobic small molecules, such as azobenzene, by regulating temperature.

COLL 525 Water-soluble and water-swellable polymeric photosensitizers

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Water-soluble and water-swellable polymeric photosensitizers were obtained by functionalization of natural polymers or thermosensitive hydrogel microspheres with aromatic chromophores such as naphthalene (Np), anthracene (A), porphyrin (Po), fluorene (Fl), chlorophyll (Cl), and rose bengal (RB). The photosensitizers based on polysaccharides (dextran, starch, chitosan) have been found to be useful in the photodegradation of the organic compounds of environmental interest such as polynuclear aromatic hydrocarbons (PAHs), pesticides, chlorinated aromatic pollutants (CAPs) as well as toxic inorganic compounds such as cyanides. Using the Zahn-Wellens test it was demonstrated that these functionalized natural polymers are biodegradable. Model studies carried out with pentachlorophenol have shown that the thermosensitive hydrogel photosensitizers composed of N-isopropylacrylamide (NIPAM) and 2-hydroxyethyl methacrylate (HEMA) can be successfully used for removal of CAPs from water both via their photosensitized degradation and by physical filtration of hydrogel microspheres in which they are solubilized.

COLL 526 Formation of nanoscale water bridges

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The water bridges provide stability to sand castles, act as transport channels for dip-pen nanolitography and increase adhesion and friction in micro- and nano- devices such as MEMS. The kinetics of capillary condensation and growth at the nanoscale is studied here using friction force microscopy and molecular dynamics calculations. At 40% relative humidity we find that the meniscus nucleation times increase from 0.7 ms up to 4.2 ms when the temperature decreases from 332 K to 299 K. The nucleation times grow exponentially with the inverse temperature 1/T obeying an Arrhenius law. We obtain a nucleation energy barrier of $7.8*10^{-20}$ J and an attempt frequency ranging between 4-250 GHz, in excellent agreement with theoretical predictions. These results provide direct experimental evidence that capillary condensation is a thermally activated phenomenon.

R. Szoszkiewicz and E. Riedo, "Nucleation time of nanoscale water bridges" Phys. Rev. Lett. 85 135502 (2005).

COLL 527 Effects of adsorbed water layer structure on adhesion force of silicon oxide nanoasperity contact in humid ambient

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The origin of the large relative-humidity (RH) dependence of the adhesion force in the single-asperity contact between silicon oxide surfaces is elucidated. As relative humidity (RH) increases, the adhesion force measured with an atomic force microscopy (AFM) initially increases, reaches a maximum, and then decreases at high RH. The capillary force alone cannot explain the observed magnitude of the RH dependence. The origin of the large RH dependence is due to the presence of an ice-like structured water adsorbed at the silicon oxide surface at room temperature. A solid-adsorbate-solid model is developed calculating the contributions from capillary forces, van der Waals interactions, and the rupture of an ice-ice bridge at the center of the contact region. This model illustrates how the structure, thickness, and viscoelastic behavior of the adsorbed water layer influence the adhesion force of the silicon oxide nanoasperity contact.

COLL 528 Environmental effects on tribological studies

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Chemical composition of the test environment has been demonstrated to play an important role in the friction and wear performance of most tribological materials. However, it is not trivial to understand the exact role of small amounts of impurities in the environment because it is difficult to create perfectly inert atmospheres. Most “inert” test environments reported in the literature are created by purging with dry N_2 to minimize H_2O and O_2 impurities. This typically results in 2 to 5% relative humidity and undetermined amount of O_2 in the test environment. We have employed an ultra-high vacuum (UHV) tribometer to systematically control and study the precise effects of these impurities on tribological performance. We have found that minute amounts of impurities, such as < ppm quantities of H_2O and O_2, significantly affect the tribological test results for a wide variety of materials, including hard coatings and solid- and liquid-lubricated steels.

COLL 529 Issues in the vapor phase lubrication of magentic data storage media

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Vapor phase lubrication offers a means for integration of media lubrication with the vacuum processing steps used to fabricate data storage media. In vapor lubrication the a-CH_x surface will have to be oxidized under controlled conditions immediately prior to lubricant adsorption. The kinetics of a-CH_x and a-CF_x oxidation have been studied extensively using XPS in an apparatus that allows oxidation of freshly deposited films. Oxidation of the fresh a-CH_x and a-CF_x surfaces is much slower than for a reactive metal surface. The dissociative sticking coefficient is $\sim 10^{-6}$ although this varies over a couple of orders of magnitude during the surface oxidation process. Lubricant adsorption during vapor phase lubrication will depend on such things as the degree of oxidation of the surface. The adsorption and desorption of model fluoroethers and fluorinated alcohols have been studied on the surfaces of fresh and partially oxidized a-CH_x films.

COLL 530 Gas-phase lubrication of silicon nano-asperity contacts

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Adhesion, friction, and wear in MicroElectroMechanical System (MEMS) devices are key challenges limiting MEMS technology. To prevent wear, a self-healing or replenishing lubricant layer is needed. The adsorption equilibrium isotherm of gas-phase alcohol lubricant molecules provides the formation of molecular-thick films on silicon oxide surfaces. The adsorption of alcohol on silicon surfaces lowers both the adhesive and frictional response between native silicon oxide nano-asperity contacts. Tribological properties of alcohol vapor films are investigated as a function of chain length (C2 – C5) on silicon contacts. Surface chemistry pertinent to this system is discussed.

COLL 531 Design of polymeric lubricant additives to reduce friction and wear

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Dissolved polymers are widely used as additives in lubricating oils in order to enhance the latters' viscosity-temperature properties. It is now recognized that if these polymers are suitably functionalized they can also adsorb on metal surfaces to provide beneficial boundary lubrication. This presentation describes a study of the film-forming, friction and wear behaviour of a wide range of polymethacylate polymers having varying functionality and molecular weight. The results are used to derive rules for the design of polymers with optimal boundary lubricating properties.

COLL 532 Reduction in viscosity and yield-stress in non-colloidal concentrated suspensions by surface modification and/or nanoparticle addition

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A custom-designed apparatus termed the Yield Stress Adaptor has been used to evaluate the effect of polymer-surfactant coatings, and the addition of nanoparticles of different size, shape and surface chemistry, on the rheological properties of large hydrophilic particulates, sand, with the aim of reducing interparticle friction forces. Experimental results show that the flow properties of sand slurries at high volume fractions of sand (> 50 %) can be significantly enhanced by adding nanoparticles, and by surface modification with polymer/surfactant mixtures. A lesser effect is observed for polymer-only and surfactant-only coated samples. X-ray photoelectron spectroscopy was used to determine the concentration of organic species at the surface. The effect of polymer/surfactant concentration, adsorption time, polymer molecular weight, as well as surfactant charge and chemical structure were also addressed.

COLL 533 Influence of dendrimer interlayers on the texture and tribology of Ta ultrathin films

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We have previously demonstrated the influence of dendrimer monolayers (D) on the tribological properties of ultrathin films of metal overlayers. For example, in cases where the overlayer metal is not adherent to the substrate, the dendrimers act as an adhesive interlayer. But nontrivial changes in such properties as hardness are also observed for the resulting metal/organic composite ultrathin film in cases where the overlayer metal is deposited in such a way that it does not destroy the dendrimer monolayer. For Ta, adherence to substrate (Si, native oxide) is not an issue, and we find that the presence of the organic layer influences the overlayer both morphologically and tribologically. The Ta/D system exhibits unusual preferred texturing along <330>, which increases

with dendrimer size (monolayer thickness). The critical load to failure in nanoscratch testing is improved for Ta/D vs. Ta alone. We seek to understand the role texture modification has on the tribological properties of the overlayer.

COLL 534 Probing the kinetics of CO oxidation over supported gold catalysts by isotopic transient analysis

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Bulk gold is normally considered to be inert in catalytic reactions. In contrast, supported gold nanoparticles have demonstrated exceptional low temperature catalytic activity in reactions such as the oxidation of CO, H2 and C3H6. Although supported Au has been the focus of many studies, the nature of the active site remains elusive. In the current work, alumina and titania-supported Au particles were prepared by a deposition-precipitation method involving HAuCl4 precursor and tested as catalysts in the low temperature oxidation of CO. X-ray absorption spectroscopy at the Au LIII edge revealed that the as-prepared samples contained cationic Au that was reduced to a predominately metallic state following treatment in He at 623 K. Scanning transmission electron microscopy showed the Au to have an average particle size of 3.3 and 2.5 nm for Au/TiO2 and Au/Al2O3, respectively. Carbon-13 isotopic transient kinetic analysis was used to explore the intrinsic turnover frequency and coverage of active carbon-containing intermediates that lead to product during CO oxidation. After correcting for CO2 re-adsorption, the intrinsic turnover frequency was found to be independent of temperature, approximately 3.4 and 2.1 s-1 for Au/TiO2 (261 – 303 K) and Au/Al2O3 (272 – 343 K), respectively. These results suggest the key step in CO oxidation over Au catalysts is activation of dioxygen, which is the current focus of our oxygen-18 isotopic transient studies.

COLL 535 True intermediates and spectators in reaction mechanisms: A kinetic and spectroscopic study

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An in-depth study of the mechanism of acetone oxidation with ozone was carried out using in situ laser Raman spectroscopy to follow the surface coverages of species derived from the oxidant and the reductant. The catalyst employed was manganese oxide because of its well-known activity in complete oxidation. Simultaneous measurements of rate and coverage in transient and steady-state mode allowed determination of the role of the adsorbed species in the reaction. Two main surface intermediates were identified, a peroxide species derived from ozone, with a band at 890 cm-1, and an adsorbed species with intact C-H bonds derived from acetone, with a band at 2930 cm-1. Quantitative TPD measurements showed that the peroxide species resides on the manganese and the acetone species is located on the silica support. A mechanism is proposed involving the migration of the adsorbed acetone intermediate from the silica support to the manganese centers where it reacts with atomically adsorbed oxygen species to form complete oxidation products.

COLL 536 Role of copper and other high temperature water-gas shift catalyst promoters

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Ferrochrome high temperature water-gas shift catalysts were prepared incorporating varying amounts of copper as a promoter. Consistent with other reports in the literature, the TPR peak for the copper-promoted catalysts shifts to lower temperatures relative to the base ferrochrome catalyst. When the promoter is added, the catalyst activity increases and the degree of self-inhibition by carbon dioxide decreases. The optimum loading appears to be of the order of 5 wt.%. Microkinetic modeling suggests that the addition of copper changes the binding strength of oxygen to the surface, and that this is responsible for the improved catalytic performance. The modeling further predicts a limit to the promotional effect as the copper loading is increased, as observed experimentally. Computational chemistry using simple cluster models probes the relationship between catalyst structure and promotional effectiveness. Generally good agreement is found between the experimental kinetics, the microkinetic models and the computational chemistry predictions.

COLL 537 Assessing the role of acidity of sulfides, oxides and USY zeolite catalysts

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Acidity plays an important role for many catalysts including sulfides, oxides and zeolite catalyst systems. For example, the surface acid sites of ultra stable Y (USY) zeolites play an important role in the catalytic activity and selectivity of hydrocarbon cracking reactions. This has motivated the search for various synthesis and modification routes of these zeolites in order to obtain the desired catalytic properties. It is, however, often not straightforward to characterize the resulting chemical and physical properties of the modified USY zeolites. In the present studies, several probe molecules of different sizes and basicity, specifically, carbon monoxide, ammonia and pyridine, were used to assess the acidic properties of different USY zeolites. The reactivity of these zeolites was evaluated by conducting standard hexane cracking and isobutane conversion tests. The results showed that both Brønsted acid site (BAS) density and BAS strength play a role in the cracking reactions. Some example of the role of acidity for sulfide and oxide systems will also be discussed.

COLL 538 Trapping of NOx on Pt/Ba/Al2O3 using simulated diesel exhausts

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The trapping of NOx was studied on a Pt/Ba/Al_2O_3 catalyst. The first step is the oxidation of NO with O_2 to form NO_2 on Pt. The turnover rate for this reaction is TOR/s^{-1} = 4.8×10^{6} exp(-Ea/RT) $[NO]^{1.12}$ $[O2]^{0.94}$ $[NO2]^{-0.87}$ with concentrations in volume fraction in the gas phase, T in K, Ea = 82.6 kJ mol^{-1}. This reaction is sensitive to the structure of the catalyst with rates increasing by at least two orders of magnitude when the Pt cluster diameter increases from 1 to 10 nm. The second step in trapping is the reaction of NO_2 with Ba compounds. A 1D finite element model of the monolith channel has been developed for both NO oxidation and NO_x storage on Pt/Ba/Al_2O_3. The model includes boundary layer mass transport to the washcoat as well as surface reaction and adsorption and, where necessary, a second diffusion layer to represent reaction in the interior of bulk phases. The model shows good consistency with experimental NO_x uptake data.

COLL 539 Nanocrystalline materials with enhanced photocatalytic activity under visible light

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The photocatalytic performance for the oxidation of toluene over WO_3-TiO_2 and MoS_2/WO_3-TiO_2 was studied under ultraviolet (UV) or visible light. These nanocrystalline materials were synthesized by conventional sol-gel preparation methods, by inverse micelles, and by incipient wetness impregnation. The photocatalysts were characterized using XRD, FTIR, UV-Visible, and Raman spectroscopy, SEM, and TEM. The photocatalytic activity of the WO_3-TiO_2 binary oxide catalysts was up to six times higher than P25 TiO_2 under either UV or visible light. More importantly our samples

are two times more active than titania under UV irradiation. This effect appears to be caused by an increase in the absorption power in the visible region. The initial photocatalytic activity increases nonlinearly with an increase in W content. Adding MoS_2 nanoparticles to the different oxides caused increases in the photocatalytic activity that went from 15% for WO_3-TiO_2 samples to 270% for the SiO_2-TiO_2 samples compared to the unmodified samples.

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