SYMPOSIUM HH

Bio-Inspired Materials–Moving Towards Complexity

November 26 – 28, 2001

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* Invited paper

SESSION HH1: BIOMINERALIZATION
Monday Morning, November 26, 2001
Independence West (Sheraton)

8:30 AM *HH1.1
CONTROL OF THE SHAPE AND STRUCTURE OF CALCIUM CARBONATE MINERALS BY ORGANISMS. Yael Levi-Kalisman, Sefi Raz, Bat-Ami Gotliv, Ingrid Weiss, Steve Weiner and Lia Addadi, Weizmann Institute of Science, Dept of Structural Biology, Rehovot, ISRAEL.

Organisms produce mineral-reinforced composite materials for different purposes. Each has a shape, structure and organization that have been optimized during millions of years of evolution. In so doing, a fundamental problem has to be solved, namely how to form skeletal parts with elaborated shapes that are incompatible with the symmetry, shape and structure of their mineralized building blocks. Calcium carbonate skeletal materials offer a range of solutions to this problem. Conceptually, the easiest manner to fill any given shape with solid material is when this has no internal order, i.e. it is amorphous. The spicules of some calcareous sponge and ascidians are composed of amorphous calcium carbonate (ACC). The same material is deposited in the first layer of the larval shells of some mollusks. It also strengthens the carapace of the crustaceans and is deposited in the leaves of plants in the form of cystoliths. The stabilization of the unstable ACC requires introducing into the hydrated phase macromolecules and other additives during deposition. Although all the above minerals are collectively named ACC, they differ, however, from each other in their short-range order. Thus, "amorphous" calcium carbonate has some structure. A different solution is to build the material as a single crystal, but deposit it from an amorphous phase, that slowly transforms in a controlled manner. The resulting single crystal assumes the shape of the initial phase. Sea urchins have adopted this solution in their larval spicules. Finally, mollusk shell nacre consists of polycrystalline aragonite formed inside a matrix composed of chitin and silk-fibroin-like proteins. We have proposed that the matrix consists of a layered chitin scaffold swollen with a silk-fibroin gel, which is first filled in by hydrated colloidal calcium carbonate. The latter then crystallizes into aragonite under the control of an assemblage of acidic macromolecules.

9:00 AM *HH1.2
NEW MATERIALS THAT MIMIC THE NANOSTRUCTURE OF EXTRACELLULAR MATRICES AND BONE. Samuel I. Stupp, Department of Materials Science and Engineering, Department of Chemistry, and Medical School, Northwestern University, Evanston, IL.

New materials designed with self assembled nanostructures that remind us of those produced by biology is a possible outcome of the current nanoscience era. In biology we see the self assembly of proteins and polysaccharides producing remarkable soft materials such as skin, wood, and cartilage, and hard ones such as bone, dentin, and enamel. Synthetic materials inspired by these extracellular matrices would require designing molecules with the capacity to form objects with at least one or two dimensions in the range 1 to 100 nanometers. It is also important to identify nanostructures that can mediate the formation of mineral phases in spatially controlled fashion. Such materials may turn out to be useful in miniaturized devices or in advanced medicine to repair humans. In this last application their role could be to carry signals or important cargo to cells so that tissues can be reconstructed or disease can be reversed. In our laboratory we have designed recently peptide amphiphiles with the capacity to self assemble reversibly in water into high aspect ratio nanofibers that mimic collagen in extracellular matrices. The molecular construct allows the multiplexing of signals to receptors on cells, and also the formation of apatite crystals oriented relative to the nanofibers in a way that mimics the nanostructure of bone.

9:30 AM HH1.3
PIECE-BY-PIECE STRUCTURE DETERMINATION OF SEQUENCE MODULES FOUND IN THE ELASTOMERIC BIOMINERAL-ASSOCIATED PROTEIN, LUSTRIN A: NEED WE SAY MORE? Brandon Wustman, Bo Zhang, Kan Zhou, Daniel Morse and John Spencer Evans, Laboratory for Chemical Physics, New York University, New York, NY.

The Lustrin A protein (144 kD) of abalone shell nacre layer represents a bold statement by Nature: put all of your eggs in one "basket". The "basket" in this case is the primary amino acid sequence: via evolution, the protein has acquired several multifunctional domains: (A) Eight Pro-rich domains (P-domains), (B) Ten Cys-rich domains (C-domains), (C) 256 residue Gly-Ser repeat, (D) 30-residue Arg, Lys, Tyr-rich domain, and (E) 24 residue Asp-containing triplet region. As shown in previous studies, the Lustrin A plays a critical role in abalone shell formation and maintaining shell integrity: the protein exhibits binding to aragonite mineral surfaces, forms protein-protein assemblies, and undergoes protein unfolding-refolding in response to elastic stretch. It is believed that each of the domains mentioned above plays some role in one or more of these functions. We have embarked on NMR and MALDI hydrogen/deuterium structural studies on several sequence regions of Lustrin A: (A) the -NVNC- consensus repeats found in the N-terminal region of the C-domains; (B) the basic 30-residue Arg, Lys, Tyr-rich domain; and (C) the 24-residueAsp-containing triplet region of the C-terminal domain. These multidisciplinary studies have revealed the following (A) The NVNC consensus repeat of the C-domain adopts a turn-like conformation stabilized by electrostatic interactions and a single hydrogen bond; similar structures have been identified in elastic proteins such as elastin, fibronectin, spider silk dragline, and sea urchin spicule matrix proteins. (B) The 30-residue domain adopts a coil-like conformation. The positively charged residues adopt a radial distribution on the polypeptide surface. This region is believed to interact with the aragonite surface, possibly via electrostatic interactions. (C) The 24-residue Asp-containing triplet region adopts an extended conformation, with loop regions localized near the Asp residues. When Ca (II) ions are introduced, the Asp-containing regions transform from a loop to an extended beta-strand configuration. Like the 30-residue sequence described in (B), above, it is believed that this region is putative mineral interaction domain. In conclusion, our structural studies confirm the complexity of the Lustrin A protein, and, indicate that various domains within this protein possess structural features that allow specialized functionality within the aba lone nacre layer.

9:45 AM HH1.4
BIOMIMETIC MINERALIZATION IN ENGINEERED VIRAL PROTEIN CAGES. Trevor Douglas, Erica Strable, Temple University, Dept of Chemistry, Philadelphia, PA; Mark Young, Debbie Willets, Montana State Univ, Dept of Plant Sciences, Bozeman, MT; Mathew Libera, Abdelaziz Aitouchen, Stevens Institute of Tech, Dept of Chemical, Biochemical and Materials Engr, Hoboken, NJ.

The coat protein of the cowpea chlorotic mottle virus (CCMV) has been genetically engineered to act as a mimic of iron biomineralization in ferritin. The modified virus coat protein assembles into a cage-like structure which catalyzes the oxidative hydrolysis and mineralization of nanoparticles of iron oxide in a spatially selective manner. In the wild type virus, RNA is packaged through complementary electrostatic interactions present on the interior surface of the protein shell. We have altered the electrostatics of the protein cage interior by site-directed mutagenesis of the coat protein subunit. The nine basic residues (lysine and arginine residues) on each subunit were replaced by glutamic acid residues yielding an assembled protein cage which no longer packages RNA. The negatively charged interior interface of the protein cage acts, like ferritin, to catalyze the oxidative hydrolysis of Fe(II) to form a ferric oxyhydroxide nanoparticle. High angle annular dark field STEM imaging of the cores and compositional mapping using spatially resolved electron energy-loss spectroscopy show that the ferric oxyhydroxide nanoparticle is encapsulated and constrained within the protein cage.

10:30 AM *HH1.5
MECHANISMS OF BIOMINERALIZATION WITH CALCIUM AND SILICON REVEAL NEW ROUTES TO HIERARCHICALLY ORGANIZED COMPOSITE MATERIALS. Daniel E. Morse, University of California at Santa Barbara, Materials Research Laboratory and the Graduate Program in Biomolecular Science and Engineering, Santa Barbara, CA.

With a precision of nanostructural control that exceeds present human capabilities, biological systems fabricate hierarchically organized mineral-polymer composites at low temperatures and near-neutral pH. Analyses of the proteins, genes and molecular mechanisms governing the formation of such composites in abalone shell and sponge biosilica reveal that the origin of both the exquisite nanostructural control and the associated high-performance capabilities of these biomaterials lies in the unique mechanisms of their synthesis. Multiple processes, each governing assembly at a specific dimensional scale, were found to operate contemporaneously to generate the hierarchical organization. In addition to the templating, epitaxy and polymer control of crystal nucleation and growth that were anticipated at the start of these studies, unanticipated new discoveries of self-assembling molecular stencils, novel self-healing energy-dispersive elastomers and structure-directing polymerization catalysts are helping to explain the fabrication and performance of biologically produced mineral-organic composites. Such counterintuitive new findings, overturning the previous paradigms concerning the mechanisms of biological fabrication with both calcium and silicon, now are leading to the development of new low-temperature biomimetic routes to the synthesis of advanced mineral-organic composites.

11:00 AM HH1.6
MODEL-BASED BIOMIMETIC NANOCOMPOSITE DESIGN:

FINITE ELEMENT ANALYSIS OF MOTHER-OF-PEARL OF MOLLUSK SHELLS. Kalpana S. Katti, Dinesh R Katti, Mohamed Matar, North Dakota State University, Dept of Civil Engineering, Fargo, ND; Jeffrey Sopp, Mehmet Sarikaya, University of Washington, Dept of Materials Science and Engineering, Seattle, WA.

We have developed a multiscale modeling approach that predicts mechanical responses of nacre, mother-of-pearl, incorporating experimentally-determined nanoscale properties into mesoscale 3D-numerical analysis. Nacre is a laminated, segmented, hybrid nanocomposite incorporating 10-20 nm-thick organic matrix film that surrounds 250 nm-thick CaCO3 pseudo-hexagonal platelets that are staggered across layers, a brick-mortar nanoarchitecture. Bulk mechanical properties (strength, toughness, controlled failure) of nacre are orders of magnitude better than most advanced ceramics and synthetic ceramic/polymer composites. Many mollusk species, e.g., cephalopods, bivalves, and gastropods, have nacre structure that has survived millions of years of evolution. Our model incorporates details of nano- and micro-structural characteristics including aragonite crystallography and morphology determined by TEM. As mechanical parameters, we use local properties of the individual components, biogenic aragonite and the organic matrix, measured by nanoindentation technique via an AFM. Using this finite element analysis-based model, we can now predict bulk properties of nacre. For example, our numerical simulations indicate that the organic layer, a molecular composite of polysaccharides and proteins, is a material of high yield strength and elastic modulus, orders of magnitude higher than those of synthetic polymers. Our simulations also incorporate the role of mechanical coupling at the organic/inorganic interface that is achieved via nanoscale asperities and chemical compatibility. Our model may have significant implications in biomimetic design of layered hybrid nanocomposites for practical engineering applications as wear resistant, impact resistant, tough, and durable materials.

11:15 AM HH1.7
EFFECT OF SULFATE CONTENT OF BIOMACROMOLECULES ON THE CRYSTALLIZATION OF CALCIUM CARBONATE. Jose I. Arias, Juan P. Wiff, Maria S. Fernandez, V. Fuenzalida, Jose L. Arias, Faculty of Veterinary Sciences, Universidad de Chile, and Center for Advanced Interdisciplinary Research in Materials Science, Santiago, CHILE.

Natural composite bioceramics such as bone, teeth, caparaces and shells contain organic and inorganic moieties, being the organic matrix components directly involved in the precise formation of these structures. The controlled synthesis of inorganic materials of specific size and morphology is a key aspect of material research. Biomimetic synthesis of calcium carbonate crystals in the presence of natural or synthetic organic templates has been intensively investigated in recent years. We have previously shown that chicken eggshell contains two main polymer sulfated macromolecules, proteoglycans, referred to as mammillan and ovoglycan which are involoved in nucleation and growth of the eggshell calcite crystals. They differ on their anionic properties due to the carboxylate and sulfate content of their glycosaminoglycan component. Based on biological and biochemical evidences, the putative role of mammillan, a keratan sulfate proteoglycan, is in the nucleation of the first calcite crystals, while that of ovoglycan, a dermatan sulfate proteoglycan, is to regulate the growth and orientation of the later forming crystals of the chicken eggshell. In this communication, a systematic study of the influence of variable concentrations of glycosaminoglycans differing in their sulfation status on the morphology, size and number of calcium carbonate crystals after crystallization on microbridges from a calcium chloride solution under an atmosphere of ammonium carbonate at different pH is presented. Depending on the pH and concentration, the variation of sulfation status drastically changed the morphology, size and number of calcite crystals. The produced calcite particles with various morphologies are promising candidates for some novel materials with desirable shape- and texture-depending properties.

11:30 AM HH1.8
TEMPLATING A POLYMER-INDUCED LIQUID-PRECURSOR (PILP) PHASE FOR BIOCERAMIC COMPOSITES. Yi-Yeoun Kim, Matthew Olszta, Philip Varona, Vishal Patel, Laurie Gower; Department of Materials Science & Engineering, University of Florida, Gainesville, FL.

Previously we have reported on the polymer-induced liquid-precursor (PILP) process, in which acidic polypeptides transform the traditional solution crystallization process to solidification of a liquid-phase mineral precursor, leading to a variety of non-equilibrium crystal morphologies. Based on similarities between calcite crystals produced by the PILP process to various calcium carbonate biominerals, we have put forth the hypothesis that this process could play a key role in the morphogenesis of biominerals. Our current efforts are directed at studying the effect of different organic substrates on templating the deposition of the mineral precursor. We have examined both templating onto solid substrates using soft lithography techniques for pattern formation, and templating free-standing films at the air-water interface using amphiphilic monolayers. In the latter case, we have found that different templates will effect the rate of transformation of the PILP phase, which is crucial for determining whether it will crystallize via an amorphous to crystalline transformation (forming crystalline films), or if it will recrystallize via dissolution (forming 3D spherulitic aggregates). For solid substrates, the technique of micro-contact printing has generated patterned calcitic films which are significantly different than the polycrystalline mats templated via the classical method of nucleation, in which continued growth leads to 3D calcite crystals of rhomobohedral habit. Our goal is to demonstrate that with the appropriate template and/or compartment, the PILP process provides a means for patterning and molding single-crystals of calcite, which can then be built into complex single-crystalline composites, similar to the biocomposite structures found in biomineralizing systems.

11:45 AM HH1.9
CONSTRUCTION OF NOVEL MOLECULAR RECOGNITION SYSTEM BASED ON SMART SELF-ASSEMBLED NANO-PARTICLE. Yukio Nagasaki, Masayoshi Akiyama, Science University of Tokyo, Department of Materials Science, Noda, JAPAN; Yuji Yamamoto, Atsushi Harada, Kazunori Kataoka, The University of Tokyo, Graduate School of Engineering, Department of Materials Science, Tokyo, JAPAN.

We have synthesized poly(ethylene glycol)/poly(lactide) block copolymers (PEG/PLA) possessing an aldehyde group at the PEG chain end and a pyrene molecule at the PLA chain end, which forms core-shell type block coplymer micelle possessing aldehyde groups on its surface. The size of the polymer micelle was ca. 20 to 40 nm, thus, the solution is totally transparent. The pyrene molecule located in the hydrophobic core, which emits excimer due to the location of the pyrene molecules in the very limited core space. The aldehyde groups on the micelle surface were converted to biotin moieties using biocytin hydrazide. When biotin-PEG/PLA-pyrene micelle was mixed with avidin under the suitable conditions, the excimer decreased effectively. This phenomenon can be explained by the interaction of avidin to biotin molecules on the micelle surface, which influence to the pyrene molecules located in the core. This can be explained as followings: due to the suppression of the mobility of the PEG chain end by the interaction with avidin, the stability of the self-assembling structure of the particle decreased to result in collapse or loosen the assembled structure, which causes decrease in the excimer emission drastically. This excimer monitoring system is anticipated for new molecular recognition system.

SESSION HH2: BIO-INSPIRED SYNTHESIS AND PROPERTIES
Monday Afternoon, November 26, 2001
Independence West (Sheraton)

1:30 PM *HH2.1
FUNCTIONAL SURFACE STRUCTURES VIA SELF-ASSEMBLY OF BLOCKCOPOLYMERS. Martin Moeller, Christoph Hartmann, Silke Riethmueller, Vanessa Z-H. Chan, Joachim P. Spatz , H.G. Boyen*, P. Ziemann*, Universitaet Ulm, Laboratory of Organic and Macromolecular Chemistry, OC III. *Laboratory of Solid State Physics, Ulm, GERMANY.

Arrays of nanometer sized metal and metal oxide clusters are generated by means of a polymer template. In the first place polymers micelles were used as nanocompartments that were loaded with a defined amount of a metal salt. Then a suitable substrate was coated by a monolayer of the micelles. Exposure to a plasma allowed to remove the polymer completely leaving back the naked metal particles firmly attached to the substrate in the same quasi-hexagonal order as in the film. The height of the clusters could be varied between 1 nm and 15 nm depending on the concentration of the metal salt. The interparticle distance could be varied between 30 nm and 170 nm. Such arrays of metal or metal oxide particles are used for catalysis, for magnetic dots but also to bind other molecules like proteins and specific ligands for biological cells in an ordered array and for patterned SAMs. Formation and compartmental localization of metallic nanodots within block copolymer micelles can be combined with a top down approach, i.e. electron beam lithography. The combination pushes the limit of standard lithography to nanometer sized pattern without special and very expensive equipment. Within a coarse prestructure, >100nm, nanoscopic metal or semiconductor particles can be positioned with a precision of a few nanometers by means of the self-assembling polymer shell. Metallic dots as small as few nanometers can be arranged in lines and as individual dots in periodic as well as in aperiodic patterns separated by micrometers. Soldering of in line arranged gold dots can lead to the fabrication of

nanoscopic lines several 100μm long. The individual points are sufficiently small to act as an anchor for individual macromolecules. In combination with the larger distances they form a new basis to address individual macromolecules optically and are of interest for the separation, location, and screening of DNA or proteins. For the interaction with biological cells, the Si substrate was passivated against cell adhesion using isocyanated functionalized star polymers (hydrogels). The image on the left (A) demonstrates that the cells are able to spread on a 100 micron thick gold line in the center but are unable to adhere on the silicon which has been passivated with the isocyanate layers. Such nanostructured patterns were chemically modified to present biological cells with areas of specific and nonspecific adhesion. Local control of the focal adhesion contacts of fibroblasts was achieved when the gold points were functionalized with molecular receptors, specifically an Arg-Gly-Asp tripeptide sequence (RGD).

2:00 PM *HH2.2
SELF-ASSEMBLY OF TRUE CATANIONIC TERNARY SOLUTIONS: FORMATION OF STIFF ICOSAHEDRA.
Monique Dubois, Thomas Zemb, Service de Chimie Moléculaire, CEA/Saclay, Gif sur Yvette Cedex, FRANCE; Bruno Demé, Institut Laue-Langevin, Grenoble, FRANCE; Thaddée Gulik-Krzywicki, Centre de Génétique Moléculaire, CNRS, Gif sur Yvette, FRANCE; Emile Perez, IMRCP, CNRS, Toulouse, FRANCE.

Proteins of virus capsids self-assemble in the form of regular hollow icosahedra. These also appear as a result of biomineralisation, but are extremely rare in mineral crystallites. However, self-assembled aggregates of icosahedral shape made of synthetic organic components such as surfactants have never been reported. We describe here self-assembled bilayer organisation in the form of hollow aggregates of regular icosahedral shape formed at certain compositions in salt-free mixtures of anionic and cationic surfactants (catanionics). The aggregates are stabilised by the presence of pores located at the vertices which are about one micron apart. The size (about 1μm) and mass (about 1010 Da) of the aggregates are larger than any known icosahedral protein assembly or virus capsid. The wall rigidity is in the range of 100 MPa (analogous to carbon nanotubes) and is due to the strong unscreened electrostatic interaction between the two oppositely charged surfactants whose hydrocarbon chains are crystallised. Electron microscopy, light-, X-ray- and neutron scattering results demonstrating the stability (in the complete absence of salt) of facetted objects in a certain region of the ternary phase diagram will be shown.

2:30 PM HH2.3
SYNTHETIC CELLS BASED ON POLYMERSOME MEMBRANES, BLENDS, ENCASED LC'S, AND RELATED BLOCK COPOLYMER AGGREGATES.
Harry Bermudez, Bohdana Discher, Paul Dalhaimer, Dan Hammer, Frank S. Bates, Dennis E. Discher, University of Pennsylvania, Philadelphia, PA.

Cell membranes generally have a substructure of crosslinked cytoskeletal components. We have attempted to mimic this with massively crosslinked, property-tunable block copolymer 'polymersome' membranes. Free radical polymerization was used subsequent to self-assembly of PEO-polybutadiene vesicles. We describe a series of such diblocks that have a hydrophilic weight fraction like those of lipids and that form robust fluid phase membranes in water. Crosslinked giant vesicles prove stable in chloroform and can also be dehydrated and re-hydrated without rendering the 10 nm thick membrane core; the results imply defect-free membranes many microns-squared in area. Surface elastic moduli as well as sustainable wall stresses up to 1000 Atm - orders of magnitude greater than any natural lipid membrane - appear consistent with strong tethering between close-packed neighbors. The enormous stability of the giant vesicles can be tuned down for application: blending in the hydrogenated analog polyethyleneoxide-polyethylethylene modulates the effective elastic constants as well as the rupture strength by orders of magnitude. Results appear consistent with rigidity percolation through a finite-layer stack of two-dimensional lattices. Moreover, below the percolation limit, a regime of hyper-instability emerges, reflecting perhaps nanoscale demixing and suggestive of the limitations encountered with low reactivity lipids. The results with membranes provide general insights into covalent crosslinking within self-assembled nanostructures. Liquid crystals, among other compounds, have been encaspulated in these vesicles and manipulated with the aim of understanding pseudo-cytoplasmic dynamics of micro-encased complex media. Emerging work on rod micelles should provide new opportunities for pseudo-cytoskeletal structuring of our synthetic cell membranes.

2:45 PM HH2.4
OPTICAL PROPERTIES OF SELF-ASSEMBLED CYLINDRICAL LIGHT-HARVESTING SYSTEMS.
Jasper Knoester, Mariusz Bednarz, Koos Duppen, Stefania Lampoura, Univ of Groningen, Materials Science Center, Groningen, THE NETHERLANDS; Siegfried Daehne, Christian Spitz, Andre Ouart, Fed Inst for Materials Research and Testing, Berlin, GERMANY.

We report on the preparation, (nonlinear) optical characterization, and theoretical analysis of self-assembled molecular light-harvesting systems. Plants and certain bacteria possess light-harvesting systems, i.e., supramolecular structures containing many chlorophyll molecules that absorb the energy of sunlight in the form of excitons and transport it with large efficiency (over 90%) to chemical reaction centers. In a quest to create artificial systems with similar or even better performance, many studies have been performed to unravel the microscopic nature and dynamics of the Frenkel exciton states responsible for this high efficiency. In particular, the circular light-harvesting complexes (LH2) of purple bacteria have been studied in detail, with special focus on the role of the circular geometry, effects of disorder, and the exciton coherence length. Inspired by the circular geometry of LH2, we have synthesized cyanine dyes that, owing to a combination of hydrophobic and hydrophilic substituents, self-assemble into cylindrical aggregates. Cyanine dyes were used, because these molecules have large absorption cross sections and strong excitation transfer interactions (stronger than chlorophyll molecules). Our cylindrical aggregates combine the circular geometry of LH2 with a second exciton propagation direction, which helps to overcome effects of disorder. In fact, nature has realized similar cylindrical aggregates as chlorosomes in green bacteria. We report on the first optical experiments on the synthetic cylinders and their interpretation based on exciton theory. In particular, we will discuss the linear absorption, circular dichroism, fluorescence depolarization, and pump-probe experiments. The experiments confirm the cylindrical shape of the aggregates, also seen in cryo-TEM pictures, and can be well explained using a Frenkel exciton model. The experiments are consistent with a cylinder circumference of 8 molecules and an exciton coherence area of about 100 molecules. The fluorescence depolarization at low temperatures suggests an unexpectedly fast transport of the energy over the cylinder.

3:30 PM *HH2.5
CONTROL OF TERTIARY/QUATERNARY POLYMER ION COMPLEX STRUCTURES OF BIPYRIDIN-ENCODED MACROMOLECULES.
C.D. Eisenbach, J.L. Kersten, K. Dirnberger, University of Stuttgart, Institute of Applied Macromolecular Chemistry, Stuttgart, GERMANY.

The transfer of principles of supramolecular organic chemistry to synthetic macromolecules opens perspectives for novel polymer materials with structures reminiscent to biopolymeric systems. This has been investigated for the copper(I) complex formation of 6,6$\prime$-disubstituted oligo(2,2$\prime$-bipyridin) (bpy) containing macromolecules. Monofunctional bis(bpy) and bpy moieties were synthesized and attached to a poly(ethylene oxide) (PEO) block. The 2-1 bpy encoded starting materials as well as the corresponding [$(bpy)_2$-bpy]-PEO diblock copolymers exhibited a recognition-directed and direction-controlled self-assembly upon complexation with Cu(I) ions resulting in well-defined dimers. The double-helical polymer-ion complex of the diblock copolymer dimers formed a microphase-separated system with ordered domaines of the bpy/Cu(I) complex blocks. The implication of these findings for the recognition of single encoded macromolecules and the generation of supramolecular objects will be discussed.

4:00 PM HH2.6
SUPERSTRUCTURES IN SWOLLEN PHASES OF CHARGED BILAYERS IN THE ABSENCE OF SALT.
Bruno Demé, Institut Laue-Langevin, Grenoble, FRANCE; Monique Dubois, Thomas Zemb, Service de Chimie Moléculaire, CEA-Saclay, Gif sur Yvette Cedex, FRANCE; Thaddée Gulik-Krzywicki, Centre de Génétique Moléculaire, CNRS, Gif sur Yvette, FRANCE.

Dilute solutions of charged lipids in the absence of salt form clear birefringent gels which cannot be easily understood as swollen smectic phases or vesicles. Binary phase diagrams of charged bilayers in low salt conditions, i.e. with a screening length superior to ten nanometers are extremely scarce in literature. The reason for that is that bilayers including a thick (>3 nm) layer of molten hydrocarbon chains, covered by a large structural charge (1 charge 5-6 nm^2) are expected to be stiff. These stiff bilayers are expected to strongly repel each other, hence producing sharp Bragg peaks. We used DOPS as model system of charged bilayers in the [L_α] state. Samples are birefringent, electron microscopy shows bilayer stacks, but the Bragg peaks in the absence of screening show only weakly. SAXS and SANS pattern show a peculiar behaviour: in a certain range of (controlled) osmotic pressure, a superstructure peak appears at low angle. We show that this peak is due to giant correlated undulations. The texture is reminiscent of the image produced by an oyster shell. We locate this "oyster" state of charged bilayers, where a superstructure coexists

with smectic layers in the phase diagram and analyse X-ray and neutron scattering in the large swelling regime.

4:15 PM HH2.7
EFFECT OF AMPHIPHILIC STAR-LIKE MACROMOLECULES ON THE VESICLE SIZE, PHASE BEHAVIOR AND STABILITY OF LARGE UNILAMELLAR VESICLES. Lotti Frauchiger, George Strauss, Kathryn E. Uhrich, Rutgers, The State University of New Jersey, Dept of Chemistry and Chemical Biology, Piscataway, NJ.

Amphiphilic star-like macromolecules (ASMs) are promising carriers for drugs because they can solubilize drugs which have a low water solubility and enhance the permeation of drugs through biomembranes. The mechanism of permeation enhancement is not yet known. The ASMs used in this study consisted of a hydrophobic core containing a phenolic unit, three sugar and 12 aliphatic C6 units. Three poly(ethylene glycol) chains with a molecular weight of 5000 each formed the hydrophilic shell. Interactions of the ASMs with large unilamellar vesicles (LUVs) of 1,2 dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) were observed by dynamic light scattering measurements, differential scanning calorimetry and leakage of 5(6)carboxyfluorescein (CF). The particle size of DPPC LUVs increased with increasing concentration of ASMs whereas the size remained constant after addition of equivalent molar amounts of the controls PEG (MW 5000) and Pluronic P85. Increasing concentrations of ASMs caused a shift of the main phase transition of DPPC LUVs to higher temperatures. A smaller temperature shift of the main phase transition of DPPC LUVs was observed with the controls. No leakage of CF from DPPC LUVs was observed in the presence of ASMs and PEG at a concentration of 100 mol % for 2 hours. In contrast, about 20 % of the total CF was released from the liposomes in the presence of Pluronic P85. The data clearly demonstrates that ASMs interact strongly with lipid bilayers without disrupting the membrane, which is in contrast to the action of Pluronic P85.

4:30 PM HH2.8
PROTEIN-NANOPARTICLE CONJUGATES: STRUCTURE AND OPTICAL PROPERTIES FOR ADVANCED MATERIALS IN ELECTRONICS AND MEDICINE. Nataliya N. Mamedova, Nicholas A. Kotov, Chemistry Department, Oklahoma State University, Stillwater, OK.

Nanoparticle-protein conjugates can result in the self-assembly of bioinspired logical devices and simplest electronic circuits. At the same time, they can also be considered for a variety of applications in medicine among which the in-vivo applications are the most challenging As a model system for complex nanoparticle supramolecules combining several functions, the conjugates of bovine serum albumin and CdTe nanoparticles capped with L-cysteine have been prepared. A one-pot glutaric dialdehyde cross-linking yields preferably albumin-nanoparticle 1:1 dyads with some amount of 2:1 assemblies. The conjugates of gold nanoparticles and antibodies were prepared by using biotin linkages yielding the similar products. Several experimental techniques demonstrated that the bioactivity of the protein units in the conjugates was retained. In both types of conjugates strong long-distance electronic interaction between the protein units and nanoparticles was observed. The optical studies revealed the efficient excitation energy transfer from the tryptophan moieties of albumin to the attached CdTe nanoparticles resulting in the significant increase of the nanoparticle emission. This effect can be considered as a fast communication link in the elementary hybrid bio/nano supramolecules.

4:45 PM HH2.9
ENZYMATIC CONTROL OF OLIGONUCLEOTIDE-NANOCRYSTAL CONJUGATES. C. Steven Yun and Geoffrey F. Strouse, University of California, Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

The two- and three-dimensional assembly of metallic and semi conducting nano-crystals, such as CdSe and gold, using both biological and organic oligomers hold potential as archetypical structure for nano-electronics as well as biological sensors. The employment of DNA manipulating enzymes holds promise for controlling the structure oligonucleotide gold conjugates thus setting the foundation of enzymatic control of biological based nanomaterials for electronics. In this presentation the manipulation of DNA-nanocrystal assemblies by DNA methylation enzymes will be shown.

SESSION HH3: POSTER SESSION
BIO-INSPIRED MATERIALS: MOVING TOWARDS COMPLEXITY
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

HH3.1
COLLAPSED HYDROGEL MAY FIND ITS FACULTY. Yukikazu Takeoka, Masayoshi Watanabe, Yokohama National University, Faculty of Engineering, Kanagawa, JAPAN.

We have already shown the molecular specific swelling change of hydrogels in accordance with the concentration of target molecules. The obtained gel was opaque having plasticity which means there exist week interactions between polymer chains and showed thermo-sensitive volume change in water. The diameter of the gels at high temperature, where the gel is collapsed state, in accordance with the concentration of target molecules becomes larger. However, the gel made by water as a solvent does not show the phenomena. Recently, we have developed gels that not only catalyze a chemical reaction but also switch their catalysis on and off in response to an infinitesimal change in solvent composition. The gel consists of two species of monomers. The major component, N-isopropylacrylamide, makes the gel swell and shrink in response to a change in composition of ethanol/water mixtures. The minor component, vinylimidazole, which is capable of catalysis, is copolymerized into the gel network. The reaction rate for catalytic hydrolysis of p-nitrophenyl caprylate was small when the gel was swollen. In contrast, when the gel was shrunken, the reaction rate increased 5times. We will report the importance of collapsed state of gels to find these new faculties.

HH3.2
DYNAMICS OF VESICLES UNDER HYDRODYNAMICAL CONSTRAINTS: MIGRATION AND TUMBLING. Thierry Biben, Chaouqi Misbah, GREPHE, Univ. J. Fourier, Grenoble I, FRANCE.

We introduce a new powerfull method to analyse vesicles dynamics under hydrodynamical constraints. The method allows to tackle various problems including vesicles filled with complex fluids, micro-hydrodynamics. We show that vesicles can migrate orthogonally to the imposed motion thanks to a viscous lift force, can undergo a tumbling transition and anlyze these motions. We compare the results with new experimental findings and discuss the implication on biological systems.

HH3.3
SIZE-SELECTIVE HYDROGENATION OF OLEFINS BY DENDRIMER-ENCAPSULATED PALLADIUM NANOPARTICLES. Yanhui Niu, Lee K. Yeung, Richard M. Crooks, Texas A&M University, Department of Chemistry, College Station, TX.

Nearly monodisperse (1.7 ± 0.2 nm) palladium nanoparticles were prepared within the interiors of three different generations of hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers. These dendrimer-encapsulated catalysts (DECs) were used to hydrogenate allyl alcohol and four a-substituted derivatives in a 4:1 methanol/water mixture. The results indicate that steric crowding on the dendrimer periphery, which increases with dendrimer generation, can act as an adjustable-mesh nanofilter. That is, by controlling the packing density on the dendrimer periphery, it is possible to control access of substrates to the encapsulated catalytic nanoparticle. In general, higher generation DECs or larger substrates resulted in lower turn-over frequencies (although some interesting exceptions were noted). Although the main products of the olefin hydrogenation reactions were the corresponding alkanes, ketones were also obtained when monosubstituted α-olefins were used as substrates. NMR spectroscopy was used to measure the size selectivity of DECs for the competitive hydrogenation of allyl alcohol and 3-methyl-1-penten-3-ol. The effect on catalytic rate as a function of nanoparticle size is also briefly discussed.

HH3.4
SELF-ASSEMBLY OF OLIGOPEPTIDE-POLY(ETHYLENE GLYCOL) DIBLOCK COPOLYMERS - TOWARDS STIMULI-RESPONSIVE DRUG DELIVERY SYSTEMS. Guido W.M. Vandermeulen, Harm-Anton Klok, Max Planck Institute for Polymer Research, Mainz, GERMANY.

It is well known that the attachment of poly(ethylene glycol) (PEGylation) to a protein stabilises the biomacromolecule and makes it better soluble in aqueous solutions. PEGylation protects a peptide from degradation in vivo because the PEG functions as a 'stealth'. Peptide-PEG hybrids can therefore be interesting compounds for the use as drug delivery systems. We designed a series of oligopeptide-PEG diblock copolymers in which the length of the two blocks was varied. As the oligopeptide segment a de novo designed coiled coil motif with the heptad repeat 'Ile-Glu-Ala-Leu-Lys-Ala-Glu' is used. The diblock copolymers were characterised by NMR, MALDI-TOF and RP-HPLC. The pH- and temperature-dependent self-assembly in aqueous solution has been investigated by circular dichroism, NMR, GPC and analytical ultracentrifugation experiments and will be described.

HH3.5
POLYPEPTIDE ULTRATHIN FILMS BY VACUUM DEPOSITION: PREPARATION AND CHARACTERIZATION. Timothy M. Fulghum, Rigoberto Advincula, Jimmy Mays, University of Alabama at Birmingham, Birmingham, AL; Hiroyuki Yamagami, Hiroaki Usui, Kiyotaka Shigehara, Tokyo University Agriculture & Technology, Tokyo, JAPAN.

Polypeptide ultrathin films covalently grafted on solid substrates have attracted considerable attention in the interfacial polymer science community over the past couple of years. The potential applications of these films ranges from applications in liquid crystal displays, biosensors, optical devices, etc.. Their study may address important biocompatibility issues. We have synthesized polypeptide ultrathin films through the use of the physical vapor deposition technique. We expect to gain better insight into the polymerization process of the NCA monomers, as well as, possible control of the secondary structure. Through use of the vapor deposition technique and the amino acid n-carboxy anhydride (NCA) benzyl serine we have been able to prepare polymeric amino acids for analysis. Benzyl serine NCA was evaporated in high vacuum at a temperature of 95-130°C. Different substrates have been used to examine the effects of chemical binding sites on polymerization and secondary structure formation. From IR-spectroscopy and optical microscopy it was evident that without a free amine initiator on the surface of the substrate, polymerization would not occur. Analysis of the films with IR and GPC were used to determine optimum deposition and polymerization conditions. The methyl peak around 3000 cm^{-1}, amide peak at1650 cm^{-1} and the carbonyl stretching at 1750 cm^{-1} evidence of the monomer are greatly reduced or disappear in the deposition range of 40-100nm/min. The molecular weight for this range is also increased over the total deposition range, however the rate of 50 nm/min gave a number average molecular weight of around 45000 showing a considerably higher degree of polymerization than any other deposition rate. Analysis of the films with RAS-IR was used to examine the secondary structure. Values of amide 1 peak at 1632 cm^{-1}, representing the carbonyl stretching, and the peak at 1530 cm^{-1}, representing the carbon nitrogen stretching, match with literature values of anti-parallel beta sheet conformation. Currently more work is being carried out in the direction of secondary structure verification, as well as, possible control of that structure. We will apply ion-assisted deposition (IAD) in vacuum. Also research into pattern formation and copolymer preparation is being investigated.

HH3.6
Abstract Withdrawn.

HH3.7
METALLIC NANOSTRUCTURES BY PROTEIN TEMPLATING. Silke Behrens, Wilhelm Habicht, Eckhard Dinjus, Dept of Technical Chemistry, Forschungszentrum Karlsruhe, GERMANY; Marina Baum, Eberhard Unger, Institute of Molecular Biotechnology, Jena, GERMANY.

Material properties strongly depend on the micro and nanostructure of the material. Colloidal particles of metals, for example, have potentially useful electronic properties that derive from their small, nanoscopic size and shape. The reason for these new properties lies in the quantum mechanical effect on the electronic energy levels - the quantum size effect. One important problem for defined material properties, however, is the controlled synthesis of monodisperse particles with defined atomic structure and surface as well as their assembly in geometrically ordered one, two or three dimensional arrays. The use of biological templates offers an alternative to conventional synthetic methods to direct the deposition and patterning of inorganic materials. Utilizing self-assembling protein systems, specifically microtubules (MT), the deposition of nano-sized inorganic materials such as noble metals can be controlled. Microtubules are hollow cylinders with outer diameters of 25 nm and lengths of several micrometers composed of 4 nm tubulin subunits. Using the periodic functional groups of amino acids on the outer surface of the microtubule wall as nucleation sites for the growth of monodisperse metal particles, ordered nanostructures are formed. Following a bottom-up approach noble metal particles in the nanometer size range are obtained by the reduction of the corresponding metal salts in the presence of the protein assemblies. Reducing palladium salts, for example, palladium particles (1 - 5 nm) are nucleated and immobilized on the tubulin lattice of microtubules.

HH3.8
MESOSCALE COARSE GRAINING - A ROUTE TO ENHANCE BIOPOLYMER SIMULATIONS. Dirk Reith and Florian Mueller-Plathe, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

This paper presents a new ansatz for modeling (bio-)polymer systems. On the methodological side, two automatic iteration schemes are introduced to systematically optimize the force field parameters of mesoscopic polymer systems: a simplex procedure and a structure-differences procedure. In this way, high resolution degrees of freedom can be eliminated out of polymer systems, allowing to model larger systems. Our studies show clearly that mesoscopic force fields are specific in terms of temperature and density and, hence, have to be re-optimized if the environmental conditions change. At the same time, estimates of the range of applicability of one parameter set can be given. In all cases, effective pair potentials turn out to be sufficient to construct a realistic mesoscale model. Coarse-grained simulations of poly (acrylic acid) are successfully matched against experimental light scattering data. For the hydrodynamic radius, the results are in excellent agreement for molar masses up to 300,000,g/mol. Preliminary results for carboxy (methyl cellulose) will also be considered in this study.

HH3.9
IN VITRO BIOSILIFICATION: PRACTICAL APPLICATIONS TO NANOTECHNOLOGY. Patrick W. Whitlock, Stephen J. Clarson, University of Cincinnati, Department of Materials Science and Engineering, Cincinnati, OH; Rajesh R. Naik, Lawrence L. Brott, Sean M. Kirkpatrick, Morley O. Stone, Manufacturing and Materials Directorate, Wright-Patterson Air Force Base, Dayton, OH.

In vivo biosilification allows marine diatoms and sponges to produce complex morphologies from silane precursors at the nanometer level. The ability to harness this process under laboratory and manufacturing conditions has numerous applications in materials science. Silaffins, a set of cationic polypeptides isolated from the diatom *Cylindrotheca fusiformis*, can generate a network of silica nanospheres when added to a solution of silicic acid *in vitro* [1]. By incorporating a short synthetic peptide derived from the Silaffin 1 (Sil1) protein of *C. fusiformis* into a monomer formulation, peptide-rich regions can be created on the surface of the bulk polymer using a holographic two-photon induced photopolymerization process. After exposing the cured polymer to a silane precursor, silica nanospheres are embedded in the peptide-rich regions resulting in a highly ordered two-dimensional array of silica spheres on the polymer backing. The diffraction efficiency of these devices increases nearly fifty-fold when compared to a polymer hologram without the silica spheres. Using the same peptide sequence we were also able to produce a variety of novel silica nanostructures. These structures range in morphology from common spheres to highly organized and complex fibrillar geometries that display remarkable organization at the nanometer size-scale. We are currently investigating the molecular orientation present in these morphologies and developing new methods to control the deposition of silica for nanoapplications.
1. N. Kroger, R. Deutzmann and M. Sumper, *Science* **286**, 1129-1132 (1999).

HH3.10
ENHANCED CYTOCOMPATIBILITY PROPERTIES OF HYDROXYAPATITE DOPED WITH TRIVALENT IONS. Elizabeth A. Massa, Elliott B. Slamovich† and Thomas J. Webster, Purdue University, Department of Biomedical Engineering and †School of Materials Science Engineering, West Lafayette, IN.

Hydroxyapatite (HA) is a bone-like ceramic used as a coating for dental and orthopedic implants. It is well known for its good cytocompatibility properties, but is limited in use due to its high solubility within the body and mechanical properties that differ from surrounding tissue and bone. The present in vitro study investigated a variety of dopants as a way to improve these problematic properties, while maintaining the good cytocompatibility properties of HA. The dopants investigated were divalent (magnesium and zinc) and trivalent (yttrium, lanthanum, and indium) ions known to substitute for calcium in HA. HA was synthesized by dripping 1 M calcium nitrate and 0.6 M ammonium phosphate into a solution of distilled water and ammonium hydroxide. Dopants, in the amount of 2 mol%, were also added during this liquid phase. The solution was stirred for 24 hours, while HA precipitated out. The solution was then centrifuged, rinsed, filtered, and dried. The resulting powder was then crushed, pressed into a cylinder, and sintered at 1100°C for 1 hour. The HA was then sterilized by autoclave and subjected to cytocompatibility tests, specifically, osteoblast (bone-forming cells) adhesion, proliferation, and the deposition of calcium-containing mineral. Previous results provided evidence that osteoblast adhesion was significantly greater ($p < 0.01$) on yttrium-doped HA as compared to undoped HA. The present study was meant to build on this finding by elucidating subsequent osteoblast functions, such as proliferation, synthesis of extracellular matrix proteins, and mineralization, on yttrium-doped HA as well as to determine if the 3 charge or the ionic size of yttrium may have attributed to this increased cytocompatibility. Dissolution rates and mechanical properties of the HA substrates were also examined.

HH3.11
SMALL DIAMETER, HIGH SURFACE ENERGY CARBON NANOFIBER FORMULATIONS THAT SELECTIVELY INCREASE OSTEOBLAST ADHESION. Rachel L. Price, Karen M. Haberstroh, Thomas J. Webster, Purdue Univ, Dept of Biomedical Engineering, W. Lafayette, IN.

The objective of the present in vitro study was to investigate the potential of carbon nanofibers (Applied Sciences, Inc.) that have nanometer dimensions similar to hydroxyapatite crystals in physiological bone. For the first time, results of this study provided evidence that the diameter of carbon nanofibers was inversely related to the adhesion of osteoblasts (the bone-synthesizing cells); specifically, osteoblast adhesion was 33% greater on 125 compared to 200 nm diameter carbon nanofiber compacts after one hour. However, changing the fiber diameters did not significantly affect competitive (such as smooth muscle) cell adhesion. Moreover, increasing the surface energy of the nanofibers decreased the adhesion of competitive cell lines but did not affect the adhesion of osteoblasts. Specifically, smooth muscle cell adhesion was 50% less on 125-150 compared to 25-50 mJ/m^2 carbon nanofiber compacts after one hour. Collectively, these results provided the first evidence that small diameter and high surface energy carbon nanofibers are novel cytocompatible biomaterials which allow for increased osteoblast adhesion and decreased competitive cell adhesion for possible improved osseointegration at the implant/bone interface.

HH3.12
Abstract Withdrawn.

HH3.13
NOVEL POLYMER AFFINITY MATERIALS FOR IDENTIFICATION OF PROTEINS IN SIGNAL TRANSDUCTION. Jan W. Thuring, Ze-Yi Lim, Stuart Conway, Andrew B. Holmes, Univ. of Cambridge, Dept. of Chemistry, Cambridge, UNITED KINGDOM; Nicholas T. Ktistakis, M. Manifava, Phillip T. Hawkins, Leonard R. Stephens, Babraham Institute, Cambridge, UNITED KINGDOM.

Analogs of dipalmitoyl phosphatidic acid (PA) and phosphatidylinositol-4,5-bisphosphate [PtdIns(4,5)P2] were synthesized and immobilized onto a solid support, Affi Gel-10, giving affinity matrices. These affinity matrices were used as "fishing lines" to identify a number of known proteins as well as a set of novel proteins which were found to bind specifically to PA. Learning from these bio-inspired materials will allow the design of protein-ligand screens for a variety of novel therapeutic areas.

HH3.14
MULTI-KILOBASE-PAIR AND CHROMOSOMAL DNA SEPARATION ON ENGINEERED INTERFACES. V. Samuilov, Y.-S. Seo, J. Sokolov, M. Rafailovich, Department of Materials Science, SUNY-SB, Stony Brook, NY; B. Chu, Department of Chemistry, SUNY-SB, Stony Brook, NY.

Molecular biology applications require long (multi-kilobasepairs (kbp) and megabasepairs (Mbp)) DNA separation. Traditionally, long DNA fragments are separated by electrophoresis in sieving matrixes (electrophoretic media), such as junction points in a gel. This process is slow and can not be incorporated into Lab-on-Chip microdevices. We have developed a new method to separate kilobase- and megabase-size DNA molecules on flat liquid-solid interfaces [1]. The critical factor that controls the fractionation of DNA on a flat solid-liquid interface is the local friction between the adsorbed DNA segments and the surface. The friction is determined by the amplitude of attractive potential within the plane of the surface, the period of the potential and the aspect ratio (ratio of the feature size of the pattern to the period). We use a diblock-copolymer system, self-assembled using L-B technique, to produce patterns at the nanometer length scale, which is not easily accessible by conventional lithography techniques. The micellar size and intermicellar distance is controlled by changing concentration of spreading solution and molecular weight of copolymer. This structure was used as a template for introducing metal nanopatterns on semiconductor surfaces by reactive ion beam etching. The thickness of patterned metal layer was comparable with the persistence length of DNA molecules. The experimental study of the influence of chemical patterning on the electrical transport of long DNA molecules on the liquid-solid interfaces is presented.
This work was supported by NSF-MRSEC Program.
[1] N. Pernodet, V. Samuilov, K. Shin, J. Sokolov, M.H. Rafailovich, D. Gersappe, B. Chu, DNA Electrophoresis on a Flat Surface, Physical Review Letters, 85, p.p.5651-5654, 2000.

HH3.15
A BIOMIMETIC MODEL OF A SPONGE-SPICULAR OPTICAL FIBER - NANOSTRUCTURE, OPTICAL AND MECHANICAL PROPERTIES. M. Sarikaya, H. Fong, B.W. Reed, N. Sunderland, B.D. Flinn, F. Ohuchi, and G. Mayer, MSE; A. Mescher, Mechanical Eng., U. Washington, Seattle, WA; E. Gaino, Instituto di Zoologia dell' Universita di Perugia, Perugia, ITALY.

Optical and nanomechanical properties of an Antarctic sponge Rosella racovitzea were determined using standard optical measurements and a depth-sensing vertical indentation system attached to an atomic force microscope, respectively. The Rosella spicules are 10-20 cm long with a circular cross section of diameter 200 - 600 mm. The spicules are composed of 2-10 mm thick layers of siliceous material that have no detectable crystallinity. Optical characterizations of the spicules have interesting optical waveguide properties, e.g., index of refraction, transmittance, and angle of acceptance. For example, index of refraction does not change through the thickness; hence, the spicules do not have graded index refraction despite the microscale layering. Furthermore, nanomeasurements through the thickness of the spicules also indicated uniform mechanical properties (nanohardness and elastic modulus) regardless of layering. Both the elastic modulus and nano-hardness values of the spicules are about half of that of either fused silica or commercial glass optical fibers. The fracture strength and fracture energy of the spicules, determined by 3-point bend tests, are several times those of silica rods of similar diameter. These sponge spicules are highly flexible and tough possibly due to their layered structure and hydrated nature of the silica. These physical characteristics may be due to a possible (protein/silica) molecular composite nature of the sponge spicules as suggested by XPS and TEM/EELS studies. The spicules offer bio-inspired lessons for potential biomimetic design of optical fibers with long-term durability that could potentially be fabricated at room temperature in aqueous solutions.

HH3.16
CALCIUM PHOSPHATE COATING ON TITANIUM PLATES BY ELECTRODEPOSITION. Masahiko Ishikawa, Kouji Nishikawa, Kensuke Kuroda, Ichino Ryoichi, Masazumi Okido and Osamu Takai, Nagoya University, CIRSE, Nagoya, JAPAN.

Calcium phosphate films were deposited on titanium electrodes cathodically from $CaCl_2 \bullet 2H_2O$ and $Ca(H_2PO_4)_2 \bullet H_2O$ aqueous solutions. In this study, H_2O_2 addition into electrolytes was applied to enhance the electrochemical process at the solution/electrode at a smaller cathodic potential than no H_2O_2 addition. Deposited films were analyzed by SEM observation and XRD. Cathodic current of the Ti electrode decreased once and increased in the solution with H_2O_2. It shows a cathodic peak at c.a. 25 min in the case of potentiostatic condition at - 0.756 V (vs. Ag - AgCl, sat. KCl). The calcium phosphate film grows mainly with the decrease in current after the cathodic peak. The characteristics for the electrodeposited film such as crystal morphology depends on cathodic potential, solution pH, deposition temperature and amount of H_2O_2 addition. Dense calcium phosphate film composed of relatively good crystalline was obtained at pH5.5 and - 0.756 V. Film adhesion on Ti appeared to be strong by peeling test. At larger cathodic potential of - 1.156 V, the film coverage on titanium plates was smaller and film adhesion was worsened. Larger cathodic polarization of more than - 1.556V was necessary to reduce water in case without H_2O_2 addition.

HH3.17
ARTIFICIAL ZONE OF CALCIFIED CARTILAGE FROM TISSUE ENGINEERING OF POROUS POLYMER/BIOACTIVE GLASS COMPOSITES. Kai Zhang, Univ of Minnesota, Dept of Chemical Engineering and Materials Science; Mary E. Grimm, Univ of Minnesota, Dept of Biomedical Engineering; Theodore R. Oegema, Jr., Univ of Minnesota, Dept of Orthopaedic Surgery and Biochemistry; Lorraine F. Francis, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

The structures and compositions of the interfaces between soft and hard tissues are complex and well designed for their functions. The interface between cartilage and bone, the zone of calcified cartilage (ZCC), serves as a good example. The ZCC attaches uncalcified cartilage to subchondral bone, transferring compressive forces and controlling the diffusion of tissue fluid. Biomaterials and artificial tissues have been developed for soft and hard tissue applications. However, developing the interface between the artificial and host tissues presents a challenge. New methods designed specifically for connecting artificial cartilage and bone are needed. One strategy is to construct an interface material performs the function of the ZCC, bonding to both artificial cartilage and bone. Porous polymer/ bioactive glass composites are candidate materials for engineering this artificial ZCC. A porous polymer matrix with large ($>100\mu m$) pores and small ($<10\mu m$) interconnected pores provides biological bonding via cell attachment and ingrowth, and fluid transfer, respectively. The polymer matrix also provides flexibility and toughness. The bioactive glass helps to encourage bonding to bone and may induce calcification. A liquid-liquid phase separation technique was used to make porous polymer/bioactive glass composites. Various porous

composites (polysulfone, polyurethane and polylactide) were prepared. The growth of hydroxycarbonate apatite (HCA) inside and on the composites after soaking in simulated body fluid (SBF) demonstrates the composites bone bonding ability. In culture, the interaction between chondrocytes and the composites indicates the potential for the composites to facilitate growth and attachment of artificial cartilage. The composites have the potential to engineer the interfaces between soft and hard tissues, e.g. the zone of calcified cartilage, ligament-bone, tendon-bone interfaces.

HH3.18
ORTHOGONAL POLYMERIZATIONS INSIDE ORDERED HYDROGELS TO GENERATE SELF-ORGANIZED NANOSTRUCTURES. Jidong He, Bing Xu, Department of Chemistry, The Hong Kong University of Science & Technology, Hong Kong, P.R. CHINA; Bingyang Du, Ophelia K.C. Tsui, Department of Physics, The Hong Kong University of Science & Technology, Hong Kong, PR CHINA.

This paper reports an "orthogonal" polymerization process to form nanostructures in pre-ordered hydrogels for the production of hierarchical materials. Our process consists of three steps: 1) organizing hydrophobic and hydrophilic monomers (e.g., norbonene or dicyclopentadiene, acrylamide, and water) into liquid crystalline phases (e.g. cubic or lamellar); 2) gelating the hydrophilic mesophase with the radical initiator to form ordered hydrogel; and 3) 'orthogonal' polymerizing the hydrophobic monomers in the mesophase to form the ordered polymer wires or sheets inside hydrogels. The diameter or thickness of the polymer is in the ranges of few nanometers. We will also describe the X-ray study and the measurement of elastic modulus of those systems. These self-assembled, ordered nanostructures should provide a new material that may serve as artificial muscles or mimic other soft tissues, which require sophisticated functions with subtle controls.

HH3.19
FORMATION OF BIOAPATITE THROUGH HYDROLYSIS OF CALCIUM PHOSPHATES. Alex Veresov, Olga Sinitsina, Natalya Plohih, Valery Putlayev, Yuri Tretyakov, Department of Materials Science, Moscow State University, Moscow, RUSSIA.

Bioceramics based on hydroxyapatite are widely used in modern medicine as implants for restoration, repairing and remodeling of living bone tissue. Many bioceramics have been developed for past decade (mainly based on hydroxyapatite - HAp) but only few of them have found a real application. It is proposed that good bonding to bone depends on stable interface between implant and tissue. A shape of the artificial apatite crystalls is believed must be closed to that of bone minerals if one would like to improve biocompatibility of bioceramics. Depending upon the technique, powders with various morphology, stoichiometry and level of crystallinity can be obtained. The main approaches of apatite preparation are wet methods and solid state reactions. During the wet methods it is necessary to control all parameters affecting the system (pH, supersaturation, impurities, T etc.). The variation of the control parameters can change a crystal habit from a needle-like shape to equiaxed particles and plates. The results of the wet preparation of the calcium phosphates under various conditions are reported and possible reasons for obtained crystal morphology are given. The HAp was synthesized through hydrolysis of $CaHPO_4$, and α-Ca_3 $(PO_4)_2$, precipitation from solutions containing Ca^{2+} and $PO_4{}^{3-}$ ions. The former reaction demonstrated extremely sluggish kinetics (<5% rate conversion of $CaHPO_4$), the later led to different phases depending on pH and supersaturation. In some cases the solutions were modified with biopolymers (gelatin, agar). The modifications dramatically influence the size and morphology of crystals. The reactions and products were analyzed with pH, pCa - measuring, XRD, SEM, TEM, chemical analysis.

HH3.20
PROCESSING, STRUCTURE AND MAGNETIC PROPERTIES OF BIOACTIVE FERROMAGNETIC GLASS-CERAMICS. Theodora Leventouri, Antonella Kis, Camelia Bunaciu, Florida Atlantic Univ, Dept of Physics, Boca Raton, FL; Korey Sorge, James Thompson, Oak Ridge Natl Lab, Oak Ridge and Univ of Tennessee, Dept of Physics, Knoxville, TN.

The initial interest in ferromagnetic bioactive glass-ceramics derived from the possibility of bonding to living bone and formation of an apatite layer on the surface of the bone in body environment. Subsequently it has been reported[1] that these materials generate heat in the presence of an ac magnetic field and show healing properti-es in hyperthermic treatment of bone cancer. In this work, we report on the synthesis, structure, and magnetic proper-ties of a series of materials in the system Fe_2O_3-CaO-P_2O_5-SiO_2. The effect of processing parameters on the structure of the material is studied in series of samples that were prepared with various starting compositions and heat treat-ment The development of the phases in the multiphase pro-ducts was studied with x-ray powder diffraction. The type and number of forming phases depends on the processing para-meters. The magnetic properties were studied with a SQUID magnetometer in applied fields to 30 kOe. Studies were conducted primarily at 300 K, but also at lower tempera-tures in selected cases. Magnetic saturation, coercive field, and hysteresis loops strongly depend on the anneal-ing temperature, starting chemical compounds, composition as well as mechanical treatment of the specimens. Correlation between processing, structural, and magnetic properties will be discussed.
1. K. Ohura, et al. J. Appl. Biomater.2, 153 (1991).
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HH3.21
SELF-ASSEMBLED MONOLAYERS FOR LATERAL DIFFUSION OF IONS AND MOLECULES. Carla E. Heitzman, Paul V. Braun, Huilin Tu, Dept of Materials Science and Engineering, Champaign-Urbana, IL.

We present a design for, and initial results on, the transport of specific molecules and ions through self-assembled monolayers; complete realization would enable advances in intercellular communication, nano-separation of chemicals and molecular logic devices. Molecules are designed to self-assemble into amorphous monolayers on gold and silicon oxide. Monolayers of thiol-terminated oligo(ethylene oxide), of about ten repeat units, were formed on gold; the molecules were synthesized to contain a carboxyl group adjacent to the thiol to frustrate crystallization of the monolayer which would likely otherwise occur upon self-assembly. (Mercaptopropyl) methylsiloxane dimethylsiloxane copolymers with 2-3% and 4-6% of randomly distributed mercaptopropyl groups were also used to form monolayers on gold; the resulting layers were amorphous. The increased free volume and mobility in these layers, vs. traditionally crystalline layers, allows for the dissolution and lateral diffusion of molecular and ionic species. This diffusion can be quantified with fluorescence and electron microscopy techniques and the physical characteristics of the layers have been investigated with elipsometry, contact angle, and scanning probe studies. Ellipsometry measurements have shown a correlation between thiol percentage and layer thickness in the siloxane monolayers: as the percentage of thiol groups increases, the thickness of the resulting monolayer decreases. Contact angle measurements with water indicate that the oligo(ethylene oxide) monolayer is hydrophilic, and thus probably amorphous because if crystalline the terminal methyl groups would be presented and the monolayer would appear to be hydrophobic.

HH3.22
ELECTROCHEMICAL SYNTHESIS OF IRON OXIDE TUBES AROUND A BUBBLING TEMPLATE. David Stone, Dept of Environmental Sciences, Ray Goldstein, Dept of Physics, University of Arizona, Tucson, AZ.

Iron(III)-based complexes can be brought out of aqueous solution by hydroxylation and will bond with each other as they precipitate and are reduced. We are studying a novel method of electrochemically amplifying this process whereby macro-scale tubular deposits are grown around bubbles of hydrogen gas evolving off a cathode. The bubbles emerge from the tops of the tubes surrounded by a film of basic solution, which reacts with the surrounding dissolved iron causing precipitation of iron hydroxides. The electron-rich double layer around the cathode apparently promotes extensive inter-molecular bonding and the resulting structural integrity allows the growth of long, thin tubes. Manipulating the external current and other factors can change the morphology of these self-organized, nano-crystalline formations. In the presence of magnetic fields their typically vertical orientation can be altered even to the point of reversing direction. We are exploring both the physical and chemical parameters of this process with the goal of more effectively controlling the growth of the tubes and their material characteristics.

HH3.23
MESOSCOPIC CHANNEL FORMATION DURING AN UNSTABLE LANGMUIR-BLODGETT TRANSFER. Kok-Kiong Loh, Avadh Saxena, Turab Lookman Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM; Atul Parikh, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM.

Rapid withdrawal of a planar solid substrate from a monolayer derivatized air/water interface has been shown to produce a characteristic patterned deposition in a recent experiment [M. Gleiche, L.F. Chi and H. Fuchs, Nature **403**, 173 (2000)]. The structure consists of alternating stripes exhibiting wettability constrast, creating a macroscopic array of micrometer-sized channels with potential micro-/nano-fluidic applications. Using a hydrodynamic description of surfactant deposition at a lateral pressure near the $L_1 - L_2$ phase transition, this spontaneous emergence of stripe

pattern can be understood as a result of the mismatch in the surfactant transfer. Approximate quantitative predictions of the criterion of channel formation, and dependence of the widths of the channels on the experimental parameters have been derived.

HH3.24
BIOACTIVE MESOSTRUCTURED SILICA COATINGS BY TEMPLATED SOL-GEL PROCESSING. Jose M. Gomez-Vega, Hiroyuki Sugimura, Osamu Takai, Department of Materials Processing Engineering, Nagoya University, Nagoya, JAPAN; Atsushi Hozumi, National Institute of Advanved Industrial Science and Technology, Nagoya, JAPAN.

Mesoporous silica films were applied on different substrates (glass, silicon, Ti, Ti_6Al_4V) by spin coating of acidic sol-gel solutions prepared with tetraethylorthosilicate as the silica precursor and amphiphilic triblock copolymers (polyalkylene oxide type) as the mesoporous directing agents. X-ray diffraction analyses indicated that hexagonally packed mesochannels run parallel to the substrate surface in a highly preferred alignment. The fact that mesoporous silica films could be prepared even on amorphous substrates like glass shows that there is no an orienteering effect of the substrate on the mesostructure growth. When the small cationic surfactant cetyltrimethyl ammonium chloride was used instead as template, the obtained films were not oriented. The formation of preferred aligned structures was related to the response of block copolymers to dynamic processes like spin-evaporation induced shear. Further, a photocalcination approach (ultraviolet irradiation) was proved to be a valid alternative to the conventional thermocalcination method to hollow the silica matrix, since it does not oxidize metallic substrates, causes less disorder of the mesostructures, and generates silanols (anchor sites to potential funtionalization of the silica films). Calcinations in oxygen plasma were also investigated to eliminate the templates. By this method, it was possible to optimize the conditions to eliminate completely the organics, although the resulting mesostructures were more distorted than by photocalcination. The mesoporous structure and the presence of abundant silanol groups may be responsible for the exhibited capacity of these coatings to form apatite when soaked in physiological conditions in a simulated body fluid. The methodology presented in this work is therefore a valid approach to fabricate silica coatings with tailored pore size range and mesochannel alignment. These features may induce the formation of preferentially ordered hydroxyapatite and collagen structures that confer to these implants unique mechanical properties and capacity of adhesion to bone.
This work is supported by JSPS-RFTF99R13101.

HH3.25
DEVELOPING A CHEMICAL MODEL FOR THE NUCLEATION OF BIOMINERALS USING LESSONS LEARNED FROM THE ANALYSIS OF NATURAL HARD TISSUES. Valiyaveettil Suresh, Rajamani Lakshminarayanan, Department of Chemistry, National University of Singapore, SINGAPORE.

Organisms are capable of developing multitude array of minerals in order to fulfill important biological functions. More often the mineral phase is intimately associated with organic macromolecules such as proteins and proteoglycans. These proteins are highly acidic in nature and have been postulated to provide nucleation site for the mineral formation. We are developing a chemical model system using synthetic polymers and macrotemplate to understand the fundamentals of biomineralization and to mimic the formation of natural hard tissues such as bones or teeth. The talk will focus on specific approaches developed in our lab and some of our recent results.

HH3.26
DEVELOPMENT OF NO-REJECTION AQUEOUS HUMOR PRESSURE CONTROL MEMBRANE IN THE EYEBALL FOR GLAUCOMA IMPLANT DEVICES. Y. Sato, M. Murahara, The Faculty of Engineering, Tokai University, Kanagawa, JAPAN; J.M. Parel, Bascom Palmer Eye Institute, University of Miami, FL.

The inner porous PTFE membrane was substituted with hydrophilic group using an ArF laser. The water was employed for defluorination agent in order to inhibit rejection. The membrane was developed that automatically pump out water when the pressure is raised above the fixed value. The increased intraocular pressure with aqueous outflow failure causes the glaucoma. In healthy human intraocular pressure is maintained at normal physiological level between 8 to 18 mmHg. When the pressure exceeds 21mmHg, a diagnostic of glaucoma may be predicted. Then, we designed new type of membrane to pump the aqueous humor and regulate its outflow was created. The membrane has gained characteristics of aqueous humor penetration by substituting a part of hydrophobic group that exists inside the porous PTFE with the hydrophilic group. Furthermore our previous studies have found that B, Al and H atoms are effective for defluorination atoms from fluorocarbon. In this study three kinds of reaction liquid containing B, Al and H respectively were used. By this defluorination reaction B and Al atoms were better than H atoms. Then we prepared boric acid water solution (B(OH)3) , sodium aluminate water solution (NaAl(OH)4) and water (H2O) as chemical compound for defluorination and OH substitution. Then the ethyl alcohol is dropped on the porous PTFE, it penetrates into inner porous PTFE easily. Then, three kinds of the chemical compound water solution is dropped onto the porous PTFE, the solution is trapped up to the inner side of porous PTFE. When each sample with hydrophilic property treatment was implanted into rabbitsf eyes and its biocompatibility was tested, some samples using Al and B atoms for defluorination have shown the rejection reaction called neoplasm blood vessel. However, the others using water as reaction liquid have shown no rejection.

HH3.27
EXCIMER LASER INDUCED HYDROPHILIC TREATMENT OF PET LIGAMENT TO INHIBIT FIBROBLAST AND COLLAGEN. H. Omuro, M. Murahara, The Faculty of Engineering, Tokai University, Kanagawa, JAPAN.

PET film surface was modified to be hydrophilic for the purpose of making the implantation of collagen readily. The PET has been widely used for medical materials such as an artificial ligament because of its strength and good immune reaction. However, when transplanted in human bodies, its compatibility is not good enough to adapt to the collagen, which grows from living body tissues. To avoid this reaction medicine has been used clinically which makes the PET fiber into a mesh state and after the transplantation into a human body, makes the tissue intrude in the PET fiber. However, this method has not shown satisfactory enough results to promote rehabilitation. If the living body compatibility of materials is improved the initial adapting power with the tissue can be enhanced. Then we substituted NH2 and OH, which has a high affinity for collagen on the PET surface by ArF laser. PET is highly hydrophobic and dose not dissolves well in aqueous solutions. To avoid this reaction we make a thin ammonia water layer on the PET surface with capillary phenomenon. Then ArF laser was irradiated vertically onto the sample. The result of this treatment shows that untreated sample having the contact angle of 80° with water and the bonding power of only 1.0 kg/cm^2 with collagen was improved to have the contact angle of 45° and the bonding power to be 6.0 kg/cm^2 after treating in ammonia water as a reaction solution. Moreover, when treated in water, the contact angle was improved to be 33° and the bonding power to be 7.5 kg/cm^2. When the treated sample had been implanted into the subcutaneous tissue of a rabbit's regiones dorsales, existence of leukocyte colonies that are sign point of histotropic was confirmed on the hydrophilic parts of the sample.

HH3.28
LOW TEMPERATURE DEPOSITION OF TRANSPARENT ULTRA WATER-REPELLENT THIN FILMS BY MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Yunying Wu, Yasushi Inoue, Hiroyuki Sugimura, Osamu Takai, Nagoya Univ, Dept of Materials Processing Engineering and Aichi Science & Technology Foundation, Nagoya, JAPAN.

Addition of water repellency to various materials such as glass, Si and plastics etc. has become increasingly important and been persistently demanded in many engineering fields. One of the most common methods for obtaining water repellency is spreading fluoropolymer of fluoroalkylsilane onto a substrate. However this method is not applicable to low heat-resistant substrates such as plastics, since the method requires the burning process after spreading which is conducted at a temperature about 600K. The objective of this stud is the preparation of ultra water-repellent and optically transparent silica films at low temperatures below 323K. The films were deposited by means of microwave plasma enhanced plasma chemical vapor deposition using organosilane, that is, trimethylmethoxysilane (TMMOS) as a source with adding a gas, that is, Ar, CO_2, N_2 or air. The partial pressure of the added gas was kept at 30 Pa throughout this study. The partial pressure of TMMOS was varied from 10 to 100Pa. Transparency of the films was more than 90% in the visible range. Water contact angles of the deposited films increased with an increase in the partial pressure of TMMOS, regardless of the added gas. As observed by FE-SEM and AFM, the surface morphologies of the deposited films strongly depended on the total pressure during deposition. The control of surface morphology is of primary importance in order to obtain ultra water repellency.
This work is supported by JSPS - RFTF99R13101 and ASTF.

HH3.29
INVESTIGATION OF LITHIUM NAPHTHALOCYANINE AS A PARTICULATE PROBE FOR BIOLOGICAL EPR OXIMETRY. A. Manivannan, Department of Physics, West Virginia University, Morgantown, WV; H. Yanagi, Faculty of Engineering, Kobe University, Rokkodai, Nada-Ku, Kobe, JAPAN; G. Ilangovan, J.L. Zweier and P. Kuppusamy,The EPR Center and Department of Medicine, Johns Hopkins University, Baltimore, MD.

Metal naphthalocanines (MNc) possess extended π-conjugation system that leads to a change in their optical, electrical, and magnetic properties. Among the MNc family of compounds, we report lithium naphthalocyanine as a potential solid-state paramagnetic probe for electron paramagnetic resonance (EPR) - based oximetric applications. The present molecule has been characterized as an aggregate of dilithium naphthalocyanine (Li_2Nc) and monolithium naphthalocyanine (LiNc) based on UV-Visible, X-ray diffraction and EPR techniques.This lithium naphthalocyanine dye aggregate can be simply represented as $[Li_2Nc(LiNc)_n]$ or Li_xNc which seems to be a suitable candidate for the determination of oxygen in vivo and in vitro electron paramagnetic resonance (EPR) oximetry studies. An oxygen-dependable peak-to-peak EPR line-width ranging from 0.50 G (at pO_2: 0 mmHg) to 26.50 G (at pO_2: 760 mmHg) has been observed. The EPR spectral characteristics, linear calibration plot for the oxygen concentration vs. line width for this material revealed the prospects as an oximetry probe for biological applications. The application of this probe has been utilized for the measurement of arterial, venous, and tissue oxygen tensions in a mouse. These results demonstrated superior properties of Li_xNc over the other particulate probes that are currently being used.

HH3.30
COMPLEX MATERIAL USING β-CYCLODEXTRIN AND NICKEL-ZINC FERRITE TO OBTAIN A MAGNETICALLY TARGETABLE DRUG CARRIER. Alberto Bocanegra, Rubén D. Sinisterra, Nelcy D.S. Mohallem, Universidade Federal de Minas Gerais, ICEx, Dept. of Chemistry, Belo Horizonte, MG, BRAZIL.

For most bioactive agents, the clinically optimal therapeutic benefits are often obtained only from very high doses or from prolonged drug exposure. However, dose limiting toxicity at critical organs other than the target limits better therapeutic performance. As strategy to overcome this problem one can use a magnetically targetable drug carrier complex materials. The main applications of magnetic carriers has been derived from the fact that specific ligands can be covalently or ionically bound to the magnetic particles. The strong binding makes the desorption of these ligands a difficult task and sometimes this approach change the biological activity of the bioactive agents. This major clinical limitation has generated interest in site-specific drug delivery systems. Cyclodextrins are potential candidates for such a role, because of their ability to include guest molecules into their cavity increasing the biological activity of the guest molecules. In this study is described the preparation and the characterization of the complex material using β-cyclodextrin covalently bound to the Ni-Zn ferrite to obtain a magnetically targetable drug carrier. The physic-chemical characterization was performed through Fourier transformed infrared spectroscopy, X-ray pattern diffractometry, XRD, thermal analysis (TG/DTG, DSC), X-ray fluorescence spectroscopy and atomic absorption spectroscopy. The results pointed out that the b-cyclodextrin is externally covalent bound to the Ni-Zn ferrite. However it was also verified that cyclodextrin cavity is free and can include bioactive agents. The most interesting features of this approach is the combination of magnetic properties and the host:guest technology to obtain an efficient targetable drug carrier system. In this multicompartment system (magnetic and restrain domains regions) can be changed a very wide variety of guests with simple preparations steps.

HH3.31
EVALUATION OF THE ADHESION, SUBSTANTIVITY AND ANTIMICROBIAL ACTIVITY OF SUPRAMOLECULAR COMPLEX: TETRACYCLINE: β-CYCLODEXTRIN OVER DENTIN SURFACE. M. Esperanza Cortés, André L. Pataro, Carolina F. Franco, Vagner R. Santos, Faculdaade de Odontologia Rubén D. Sinisterra, Departamento de Química Universidade Federal de Minas Gerais, Belo Horizonte, BRAZIL.

A biochemical approach to periodontal regeneration has used partial demineralization of the root dentin surface with tetracycline. Tetracycline is substantive, binding to dentin surface, while retaining its antimicrobial activity. The aim of this study was to evaluate the substantivity, superficial effect, and antimicrobial activity over bovine roots of inclusion compound tetracycline: -cyclodextrin (TC:BCD). Desorption of tetracycline from the slab was measured in the solution samples by ultraviolet visible spectra. The morphological effects of tetracycline were determined by scanning electron microscopy. Antimicrobial activity was determinated by Minimum Inhibitory Concentration (MIC) on 24 hs culture of Actinobacillus actino-mycetemcomitans (A.a) Y4-FDC. The inhibition of bacterial growth was assessed by spectrophotometric mesurement. Our results indicate that the use of TC:BCD solution release from dentin retained antimicrobial activity on A. actinomycetemcomitans with a MIC 2% containing 6.4 mg of free tetracycline. The tetracycline encapsulated in -cyclodextrin maintained the substantivity inherent of free tetracycline. Desorption in a discontinuous flow assay maintained biologically active concentrations of TC in the fluid phase for at least 96 hours. The TC:BCD SEM shows that it cause a light demineralization on the dentine surfaces over 5 days after in comparison with the free tetracycline. The dentine pigmentation was time dependent and less evident in a TC:BCD group rather than free TC. The interaction inclusion compound-dentine promote more amorphous phase as compared to crystalline one observed in the tetracycline-dentine complex. In conclusion, the tetracycline: -cyclodextrin inclusion compound bonding from the dentin surface lets release of active drug. The degree of adhesion between TC:BCD and dentine seems to influence the antimicrobial activity and visible pigmentation.

HH3.32
A BIOCOMPATIBLE STUDY OF CHRONIC IMPLANTS FOR ELECTRICAL STIMULATION AND CHEMICAL DRUG DELIVERY. Claudine A. Jaboro, Mona R. Safadi, Alexander L. Lagman, Gregory W. Auner, Department of Electrical and Computer Engineering/Biomedical Engineering, Wayne State University, Detroit, MI; Gary Abrams, Raymond Iezzi, Pat McAllister, School of Medicine, Kresge Eye Institute, Department on Neurosurgery, Ligon Center for Vision, Wayne State University, Detroit, MI; Ratna Naik, Department of Physics, Wayne State University, Detroit, MI; Vaman M. Naik, Department of Natural Sciences, University of Michigan-Dearborn, MI.

This study examines the development of chronic implants using AlN wide band gap semiconductor devices for electrical stimulation and chemical drug delivery to neural tissue. The main focus is to test the biocompatibility and subsequent interaction between neural tissue and the device itself. Both confocal optical microscopy and Raman spectroscopy methods will be used to determine tissue status and biocompatibility between the phantom device materials and the neural brain and retinal tissue. The chronic implant device will be tested for material degradation using various characterization methods such as x-ray diffraction, atomic force microscopy and high-resolution transmission electron microscopy.

HH3.33
SYNTHESIS OF AMPHIPHILIC, STAR-LIKE MACRO-MOLECULES AS DRUG DELIVERY SYSTEMS. Lu Tian, Kathryn E. Uhrich, Rutgers University, Dept of Chemistry and Chemical Biology, Piscataway, NJ.

Because of their unique structure and properties, amphiphilic star-like macromolecules (ASMs) are being investigated for drug delivery applications. The core-shell, amphiphilic structure of this nanoparticulate system is covalently linked, which makes it thermodynamically stable as opposed to conventional micellar systems. Previously, aromatic cores were incorporated within the ASM structure but proved to be cytotoxic upon degradation. In this work, the synthesis of novel aliphatic-based ASMs from pentaerythritol tetrakis(3-mercaptopropionate), mucic acid, fatty acids and poly(ethylene glycol) (PEG) will be discussed. The polymer's core, which consists of pentaerythritol derivatives, provides a flexible, hydrophobic environment for drug encapsulation, whereas the PEG shell provides excellent water solubility. Significantly, all components are biocompatible and the linkages are either ester, thiol ester or amide bonds to enable biodegradation. The polymers were characterized by nuclear magnetic resonance spectroscopy, infrared spectroscopy and gel permeation chromatography as well as differential scanning calorimetry.

HH3.34
APPLICATION OF ELECTROSPINNING TO DEVELOPMENT OF A MICRO-AIR VEHICLE WING. Kristin J. Pawlowski, Ji Su, David L. Raney, Emilie J. Siochi, Joycelyn S. Harrison, NASA, Langley Research Center, Hampton, VA; Gary L. Bowlin, Virginia Commonwealth University, Richmond, VA.

Electrospinning produces fibers having diameters in the range of hundreds of nanometers to a few microns. In the last twenty to thirty years, there have been many investigations into the types of materials that can be spun into fibers using this process. Recently, the focus has moved towards refinement and analysis of this fabrication method, as well as finding broader applications for the technique. The work presented here is focused on utilizing electrospinning to produce lightweight, responsive wings for micro-air vehicle (MAV) designs. Electrospinning of electroactive polymers is of particular interest in the MAV application because it provides a mechanism for obtaining tailored fibers that can be controlled for flight adjustments such as turns and elevation changes. Fine control can be achieved by controlling fiber orientation resulting from electrospinning. The electrospun wing simulates muscle actuation that closely mimics the performance of a bird or bat wing. Various electroactive polymer blends have been electrospun. The properties of the polymer blends,

electrospun fibers, and fiber mats have been evaluated using standard techniques to determine the most appropriate polymer for the application. The electrospinning technique and experimental set-up have also been modified to facilitate fiber orientation, eventually leading to fine control of the complete wing.

HH3.35
BIO-INSPIRED SELF-ASSEMBLED "ELECTRICALLY WIRED" ENZYME MULTILAYERS IN REAGENTLESS BIOSENSORS. Ernesto J. Calvo, Claudia Danilowicz, Erica Forzani, Alejandro Wolosiuk, Marcelo Otero, INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, ARGENTINA.

Layer-by-layer supramolecular structures composed of alternate layers of negatively charged enzymes like glucose oxidase (GOx) and cationic redox polyelectrolyte such as Os-derivatized polyallylamine (PAH-Os) have been assembled. Spatially ordered enzyme and redox polyelectrolyte assemblies offer several advantages over the same systems entrapped in random hydrogels to understant the process of molecular recognition and electrical signal generation in biosensor devices. The build up or organized multilayers has been achieved by alternate electrostatic adsorption of GOx and PAH-Os onto thiolated Au surfaces with mercapto-propane sulfonate (MPS). The redox polyelectrolyte acts as a "molecular wire" that connects the enzyme FADH2 active site to the current collector electrode. In previous communications we have reported how the "electrical wiring" efficiency depends on the multilayer architecture and structure. The present communication reports on the combination of thickness shear mode resonator (EQCM) with electroacoustic impedance analysis at 10 MHz, ellipsometry and enzyme electrocatalysis measurements to study the build-up and behavior of these self-assembled multilayers. Upon change of redox state in the Os(II/III) polymer by electrochemical perturbation, the thickness and viscoelastic properties have been followed simultaneously to the current-potential and current-time evolution. For films which resulted acoustically thin, the mass change due to the exchange of ions and solvent with the external electrolyte was correlated to the amount of electrical charge and the nature of the overal process unravelled.

HH3.36
FORMATION OF SUPRAMOLECULAR ASSEMBLIES BY MODULATING SELF-ASSEMBLING PROPERTIES OF DIACETYLENIC PHOSPHOCHOLINES. Alok Singh, Mark S. Spector, Joel M. Schnur, Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington, DC.

Considerable efforts have been devoted to understand transformation of microscopic morphologies in bilayers membranes derived from phospholipids. Diacetylenic moieties incorporated in the acyl chains of a phospholipid are known to lead to the transformation of multi-lamellar vesicles into tubular and helical morphologies. Previous efforts were focused on the synthesis and application of microtubules derived from charge neutral, polymerizable phospholipid, 1,2 bis (tricosa-10, 12-diynoyl)-sn-glycero-3-phosphocholine. We have been able to modulated morphologies of self-assembled structures by making small chemical changes in the vicinity of diacetylenic functionality via chemical or physical means. One such modulation has led to the synthesis of nanotubules (~45 nanometer diameter) and nanohelices. For the first time CD spectroscopy turned out to be an efficient technique to differentiate between nano and microtubules, because of remarkable changes that occurred when nanostructures transform into microostructures. We have also observed faster photopolymerization in nanostructures as opposed to their micro counterpart suggesting a different molecular arrangement in the supramolecular architecture. Polymerization renders diacetylene-based morphologies physically stable and help in performing chemistry at their surface to make them technically attractive. We will discuss synthesis and characterization of nanotubular and helical supramolecular assemblies.

HH3.37
FORMATION OF ORIENTED CALCIUM PHOSPHATE STRUCTURES ONTO SELF-ASSEMBLED TEMPLATES BY A SOLUTION-FORMED NUCLEUS MECHANISM. Barbara J. Tarasevich, Shari Li, Pacific Northwest National Laboratory, Richland, WA; David L.Allara, Pennsylvania State University, University Park, PA.

The nucleation and growth of calcium phosphate is of great importance to the formation of mammalian hard tissue structures such as bone and teeth and for unwanted, ectopic calcium phosphate deposition on arteries and implants. In spite of its importance, the mechanisms of nucleation and growth of calcium phosphate are not well known, but are believed to involve an organic template. The nucleation and growth of calcium phosphate was studied onto model nucleation templates composed of alkanethiol self-assembled monolayers on gold that were developed and tailored to have various surface functionalities, various surface site densities composed of mixtures of two thiols, and various degrees of conformational disorder composed of mixtures of SAMs of various chain lengths. Growth was studied from physiological solutions as well as simpler solutions. Kinetic studies using an in-situ microbalance, adsorbate studies using X-ray photoelectron spectroscopy, and solution studies reveal that significant nucleation and growth of calcium phosphate onto SAMs involved the adsorption of solution-formed critical nuclei. Plate-like apatite was formed with (0001) orientation. A very small degree of heterogeneous nucleation occurred in an initial slow growth induction period. Implications of the solution-formed nucleus mechanism on biomineralization, on orientation, and on the synthesis of complex calcium phosphate structures will be discussed.

HH3.38
IN-SITU OBSERVATION OF NUCLEATION AT INTERFACES: SYNCHROTRON X-RAY STUDIES OF BIOMIMETIC MINERAL SYSTEMS. Elaine DiMasi, Brookhaven National Laboratory, Upton, NY; Vishal M. Patel, Laurie B. Gower, University of Florida; Jane Bearinger, ETH Zürich; Christine Orme, Lawrence Livermore National Laboratory, Livermore, CA.

A central question in biomineralizing systems concerns the crystallinity at very early growth times, information which is out of the reach of many ex-situ observations and bulk chemical techniques. We will demonstrate the suitability of synchrotron x-ray scattering to study mineralizing interfaces. The first example system is the chemically controlled growth of calcium phosphate on titanium oxide substrates, motivated by bone implant materials. The second study presented is of mineralization from solution onto Langmuir films: for two very similar calcium carbonate forming recipes, we show that the effect upon a fatty acid monolayer's two-dimensional crystal structure is dramatically different. These observations should fuel the already vigorous debate about when an organic matrix can or should be considered a "template" for mineral nucleation.

HH3.39
IN VITRO STUDIES OF THE FORMATION OF SPHERICAL GRANULES OF CALCIUM PYROPHOSPHATE. Paul O'Brien, Ombretta Masala, University of Manchester, Manchester, UNITED KINGDOM.

The detoxification of heavy metals such as iron, manganese and zinc by marine invertebrates in part involves the formation of spherical granules, which are usually derived from calcium pyrophosphate. On the basis of various observations, it has been proposed that the formation of these granules in intracellular membrane-bound compartments is responsible for their specific composition and crystallographic form. However, the factors that control their properties and the mechanism involved in their formation are poorly understood. Zinc is a common metal ion in the granules of many organisms; in particular, marine invertebrates have a high capacity to accumulate this metal. Zinc is smaller than calcium and might be thought to replace calcium in calcium pyrophosphate with no dramatic effects on the structure. In order to clarify the effect of zinc on calcium pyrophosphate precipitation, we have studied the formation of the parent binary materials and related ternary composition in vitro. The formation of calcium and zinc doped calcium pyrophosphate by the diffusion of aqueous solutions across a tubular, semi-permeable membrane has been studied. The experiments were carried out at 25°C and pH 7, using different molar ratios of zinc/calcium. The solid products were characterised by X-ray diffraction, transmission and scanning electron microscopy, X-ray energy disperse analysis, infrared spectroscopy and thermo-gravimetric analysis. Zinc ions have been found to have a striking influence on the morphology and crystallinity of precipitates of calcium pyrophosphates. The undoped particles are observed in the form of small crystals as discrete orthorhombic plates. The doped material is characterised by agglomerates of amorphous spherical particles. Our observations suggest that the control of diffusion of the ions, rather than the complexity of the biological system, can regulate the morphology of these compounds.

HH3.40
DEVELOPMENT OF VINYL ETHER LIPIDS FOR PHOTOTRIGGERABLE FIBRINOGEN HYDROGELS. Junhwa Shin, David H. Thompson, Pochi Shum, Zhi-Yi Zhang, Purdue Univ, Dept of Chemistry, West Lafayette, IN.

We have developed an extension of the "cascade" triggering method[2] for producing rapidly gelating fibrinogen-based protein hydrogels using photosensitive calcium-loaded liposomes that is similar in concept to a system reported by Westhaus & Messersmith[3]. Interdigitation-fusion liposomes (IFL), comprised of 38 mol% diplasmenylcholine (DPPlsC), 57 mol% disteroylphosphatidylcholine (DSPC), and 5 mol% bacteriocholorophyll (Bchl), were used to encapsulate 10mM $CaCl_2$. Continuous irradiation (800nm,

400mW/cm^2) of these liposomes under aerobic conditions lead to the photooxidatively-induced leakage of greater than 90% of entrapped Ca^{2+} within 40 minutes. Mixtures of Ca^{2+}-loaded IFL, fibrinogen, and a Ca^{2+}-dependent transglutaminase enzyme remained fluid in the dark, but gelled rapidly when irradiated in the presence of air at 800nm and 37^{c}ireC. SDS-PAGE analysis of the reaction mixture showed that gelation was due to transglutaminase-mediated crosslinking of the fibrinogen α- and γ-chains. CryoSEM analysis of the resulting hydrogels revealed a sponge-like network structure with pore diameters ranging between 4-8 μm and pore walls of 0.1-1μm thickness. Photoresponsive liposomes based on more readily prepared plasmenylcholine precursors[4] can also be used to activate this system. Potential applications of this phototriggerable hydrogel system in drug delivery will be discussed.

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HH3.41

DEGRADATION STUDY OF AMPHIPHILIC STAR-LIKE MACROMOLECULE. Jin Wang, Kathryn Uhrich, Rutgers University, Dept of Chemistry, Piscataway, NJ.

The amphiphilic star-like macromolecules (ASMs), currently investigated for drug delivery application are designed to be core-shell, amphiphilic macromolecule nanocarriers. Linked by ester and amides bonds, which are susceptible to hydrolysis, ASM's are thermodynamically more stable than conventional micelles. They are also biocompatible and biodegradable, meeting the requirements for drug delivery materials. In this study, the degradation of ASM's were investigated at 37°C in a sodium phosphate buffer solution at pH=7.4 in the presence of cholinesterase, (E.C.2.4.2.7) acetyl type, a blood enzyme. Both high performance liquid chromatography (HPLC, UV detector) and gel permeation chromatography (GPC, refractive index detector) were used to observe the degradation products. Poly(ethylene glycol)(PEG MW 5000) was the first polymer degradation product observed by GPC after 16 hr. No further degradation products were detected after 48 hr. From this study, it appears that our ASMs can release the encapsulated drugs gradually until polymer degradation begins, which means the ASMs can be good candidate for drug release material.

HH3.42

FLUORESCENT SILICA NANOPARTICLES FOR SINGLE PARTICLE TRACKING EXPERIMENTS ON RAT MAST CELLS. Hooisweng Ow, Dept. of Materials Science & Engineering; Mamta Srivastava, Dept. of Chemistry & Chemical Biology; Daniel Larson, Watt W. Webb, Dept. of Applied and Engineering Physics; Barbara Baird, Dept. of Chemistry & Chemical Biology; Ulrich Wiesner, Dept. of Materials Science & Engineering; Cornell University, Ithaca, NY.

Single particle tracking (SPT) has been developed in recent years to evaluate lateral diffusion of individual components on cell surfaces. This method is based on direct observation of bright fluorescent probes that are specifically conjugated to macromolecules of interest. Tracking of individual components reveals a variety of interesting behaviors including confinement to a small region or movement along a track. This detailed information is necessary to understand how components interact within cell membranes. However, the method depends critically on the quality of the probes. The fluorescent particles must be very bright and they must be conjugated specifically to the component of interest. A major problem to overcome is nonspecific binding of the particles to cells. Silica-based nanoparticles have been demonstrated to be biocompatible and minimize non-specific binding. This study examines the synthesis and characterizations of fluorescent silica nanoparticles in various sizes suited for SPT experiments. The sol-gel synthetic protocol is based upon a well-established technique first reported by Stoeber et al, with appropriate modifications to covalently attach organic dye molecules of interests to the silica precursor. Nanoparticles of various diameters can be synthesized with narrow size distribution. More importantly, the versatility of the synthesis route allows for the incorporation of different dyes, depending on the applications of the nanoparticles. Surface functionalization studies enabling the conjugation of specific antibodies and proteins onto the fluorescent probes for specific SPT experiments will be shown. Results demonstrate the successful synthesis and systematic size reduction of silica nanoparticles down to 70 nm. Specificity studies utilizing a rat basophilic leukemia (RBL) mast cell model system will be described, revealing the promising specific binding characteristics of silica-based nanoparticles. First results of SPT experiments on the cell model system will be reported.

HH3.43

STRUCTURAL AND BIOPHYSICAL STUDIES OF REPLACEMENT LUNG SURFACTANTS. Heidi Warriner, Junqi Ding, Joe Zasadzinski, Chemical Engineering Dept, UCSB, Santa Barbara, CA; Alan Waring, Research and Education Institute, Harbor-UCLA Torrance, CA.

Human lung surfactant is a complex mixture of lipids and proteins that forms a monolayer at the alveolar interface. This monolayer modulates the surface tension of the lung, stabilizing alveoli against collapse during expiration and minimizing the work of expanding the alveolar surface during inhalation. Neonatal Respiratory Distress Syndrome (NRDS), caused by the absence of lung surfactant in premature infants, can be treated via transbronchial installation of replacement surfactant. However, Adult Respiratory Distress Syndrome, which is associated with the presence of excess blood proteins in the lung, cannot be successfully treated with existing surfactants. Previously, we showed that physiological concentrations of serum proteins can inactivate lung surfactant by holding interfacial pressure above the critical respreading pressure of a collapsed lung surfactant monolayer, preventing regulation of the interfacial tension. Combining Langmuir isotherms and fluorescence microscopy, we demonstrate that it is possible to reduce inactivation by adding modest amounts of inverse phase-forming lipids. We discuss the improved performance in the light of structural changes induced in replacement lung surfactant by the new lipids.

HH3.44

IMAGING OF SUBSURFACE DEFECTS IN BIVALVE MOLLUSK SHELLS BY PHOTOTHERMAL TECHNIQUES. Octavio Gomez-Martinez, Miguel Zambrano-Arjona, J.J. Alvarado-Gil, Cinvestav Unidad-Merida, Dept of Applied Physics, Merida, Yucatan, MEXICO.

The potential of photothermal radiometry for the subsurface defects imaging in bivalve mollusk shells of Crassostrea virginica and Ischadium recurvum is explored. It is shown that using an amplitude modulated Argon laser beam, it is possible to obtain photothermal subsurface images, detecting the infrared radiation due to the local heating of the shell. Our data are interpreted, taking into account that the signal is a combination of the effect of the infrared radiation due to the material structure and the reflectivity of the material surface. In the case of long thermal diffusion length, it is shown that the technique can be useful in the study of buried defects in the shell. The application of this technique in the monitoring of living organisms is discussed.

HH3.45

TEXTURIZATION ANALYSIS BY X-RAY DIFFRACTION OF THE SHELL OF THE MUSSEL ISCHADIUM RECURVUM (RAFINESQUE, 1820) (MOLLUSCA BIVALVIA). Daniel Aguilar, Octavio Gomez-Martinez, Juan J. Alvarado-Gil, Patricia Quintana, Cinvestav Unidad-Merida, Dept Applied Physics, Merida, MEXICO; Dalila Aldana-Aranda, George Zamora, Cinvestav Unidad-Merida, Dept of Sea Resources, Merida, MEXICO.

X-ray diffraction analysis of the texturization development of the shell of the mussel Ischadium recurvum (Rafinesque, 1820), in different growing stages is presented. Both shell faces have been analysed, which are formed basically by texturized calcium carbonate, and composed in the interior side by aragonite and in the exterior part it is mainly made of calcite. The texturization grade of the internal face of the shell has been quantified using the relative texture coefficient. Our results indicate a strong orientation from the early stages of growth, evolving when the mollusk grows, mainly in the crystallographic directions [001] and [111].

HH3.46

BIOMIMETIC MINERALIZATION OF TYPE-I COLLAGEN. Matthew Olszta, Dong-sik Kim, Elliot Douglas, and Laurie Gower, Department of Materials Science and Engineering, Gainesville, FL.

In order to produce novel biocomposites, such as bone graft substitutes, for critical-sized osseous defects, our strategy is to first gain insight as to how nature builds such exquisite biomineral composites, and then attempt to mimic those mechanisms. Our research attempts to achieve both of these requirements simultaneously, as we hypothesize that a novel polymer-induced liquid-precursor (PILP) mineralization process may be a viable mineralization mechanism in bone, while at the same time providing us with the ability to produce an advanced bone graft substitute that would be both biosorbable and load bearing. Through the novel PILP mineralization process, we postulate that intrafibrillar mineralization of collagen fibrils can be accomplished, leading to the high mineral loading achieved in bone. We have first examined mineralization of collagen with calcium carbonate because we currently have the capability to fully generate a liquid-phase mineral precursor in this

system. Concurrent studies are aimed at forming a liquid-phase mineral precursor in other systems, such as calcium phosphate, which we ultimately plan to use for generating hydroxyapatite-collagen composites. Using collagen fibers from bovine Achilles tendon (0.5-2.0mm in diameter), we have deposited calcium carbonate tablets and films on the surface of the fibers. The tablets, which are approximately 20 to 30μm in diameter, and half a micron thick, appear to be aligned in rows perpendicular to the c-axis of the collagen fibers. In subsequent studies, the reduction of the collagen fiber size to 20-100μm produced calcium carbonate films that covered the fibers, but were comprised of micron sized crystals resembling the traditional rhomobohedral calcite morphology. Continuing research is also being performed on various other type-I-collagen, including collagen sponges and tendons from domestic turkeys (which mineralize naturally). In the latter case, our goal is to mimic the nanostructure in biological systems (i.e. aligned and oriented nanocrystals).

HH3.47
MECHANISM OF PHOTOCHEMICAL CALCINATION OF SURFACTANT TEMPLATED THIN FILM SILICA MESOPHASES. Andrew M. Dattelbaum, Meri Amweg, Julia D. Ruiz, Laurel E. Ecke, Andrew P. Shreve, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM; Atul Parikh, Department of Applied Science, University of California, Davis, CA.

We have probed the evolution of structural and morphological characteristics of surfactant-templated thin film silica mesophases using a combined application of in situ FTIR, single wavelength ellipsometry, and X-ray diffraction. The latter mesophases were produced by a previously reported evaporation induced self-assembly process involving hierarchical organization of organic surfactant and inorganic silica building blocks. Briefly, oxidized silicon and gold substrates were drawn at 25mm/min from a sub cmc solution mixture containing an ethylene-oxide surfactant as a structure-directing agent, and TEOS, a silica precursor. We observe that surfactant removal, silicate reconstruction, and film shrinkage occur gradually and concomitantly. Taken together, our data indicate that the initial hexagonal phase transforms into a cubic phase through a synergistic cooperativity of the above three processes. Our recent experiments demonstrating the ability to confine photocalcination laterally further suggests that simultaneous presence of UV and ozone is optimally needed for efficient photocalcination. Systematic studies of other experimental variables, for example pulling speed and humidity, which influence film thickness and structural order, are in progress.

HH3.48
INCORPORATION OF POLYSTYRENE SPHERES IN SPRAY-DRIED PARTICLES INCREASES THEIR POROSITY. Nicolas Tsapis, Dave Weitz, DEAS, Harvard University, Cambridge MA; David Edwards, Advanced Inhalation Research, Cambridge, MA.

We have spray dried a solution of lipids and polystyrene (PS) spheres. Spray-drying the solution of lipids without polystyrene beads leads to particles with an aerodynamic radius between 2 and 3 microns, as measured by an Aerosizer, whereas the geometric radius, as measured by light scattering, is around 5 microns. The geometric size of the spray-dried particles increases as PS spheres are added to the sprayed solution, with concentrations up to nearly 80% (spheres, relative to other solutes in solution). On the other hand, the aerodynamic diameter remains relatively constant, meaning that the particle porosity is increasing. This increase has been found independent of the spheres radius. SEM experiments show that the structure of the spheres is conserved in the spray-dried particles.

HH3.49
INFRARED SPECTROSCOPY CHARACTERIZATION OF MARINE SHELLS. Octavio Gomez-Martinez, Daniel Aguilar, Patricia Quintana, Juan J. Alvarado-Gil, Cinvestav-Unidad Merida, Dept Applied Physics, Merida, MEXICO; Martin Yanez-Limon, Laura Diaz-Flores, Cinvestav-Unidad Queretaro, Queretaro, MEXICO; Dalila Aldana, Cinvestav-Unidad Merida, Dept Marine Resources, Merida, MEXICO.

Fourier Transform infrared spectroscopy has been employed to study the shells of two kind of mollusks, american oysters (Crassostrea Virginica) and mussels (Ischadium Recurvum). It is shown that it is possible to distinguish the different calcium carbonate lattice vibrations in each case. It is shown that the mussel presents mainly the aragonite vibration frequencies and the oyster the ones corresponding to calcite. The superposition, shift and broadening of the infrared bands are discussed. The change in the vibration modes due to successive thermal treatments is also reported.

HH3.50
X-RAY REFLECTIVITY AND GRAZING INCIDENCE DIFFRACTION STUDIES OF CALCIUM CARBONATE THIN FILMS FORMED UNDER COMPRESSED MONOLAYERS. Vishal Patel, Matthew Olszta, Laurie Gower, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL; Elaine DiMasi, Brookhaven National Laboratory, Dept of Physics, Upton, NY.

The deposition of calcium carbonate crystals under monolayers of various types has been studied considerably. In this study, we examine the surface-induced deposition of calcium carbonate thin films via a Polymer-Induced Liquid-Precursor process (Gower, 2000) in situ using X-ray Reflectivity and Grazing Incidence Diffraction techniques at the National Light Synchrotron Source at the Brookhaven National Laboratory in Upton, NY. Two methods of film formation are employed. The first includes the diffusion of ammonium carbonate into a solution of calcium chloride, magnesium chloride, and a soluble acidic polymer. The second method is via carbon dioxide escape from supersaturated calcium bicarbonate solutions containing a soluble polymer. In both cases, solutions were placed in a Langmuir trough, and a monolayer was spread onto the surface and compressed to a particular surface pressure. We are looking at the effect of an acidic polymer on the deposition of the calcium carbonate film at the air-liquid interface, and determining the effect of both the polymer and the monolayer characteristics on the rate of film deposition and of amorphous to crystalline transformation.

HH3.51
PATTERNED CALCITE FILMS FROM A POLYMER-INDUCED LIQUID-PRECURSOR (PILP) PHASE USING MICRO-CONTACT PRINTING. Yi-Yeoun Kim, Laurie Gower, Department of Materials Science & Engineering, University of Florida, Gainesville, FL.

An important feature of biological crystallization is perfectly orchestrated control over the microenvironment of crystal growth. In fact, certain organisms have evolved the ability to produce organized crystal arrays, which can be sequentially deposited into hierarchical composite structures with great fidelity. Control over crystallization is a critical requirement in the fabrication of advanced inorganic and composite materials. In principle, the synthetic growth of crystals can be guided by molecular recognition at interfaces, as occurs in biomineralization. Precise localization of particles, nucleation density, size and morphology are important parameters that affect the performance of inorganic materials, yet rarely can control over all of these properties be accomplished in one synthetic system. We propose that a polymer-induced liquid-precursor (PILP) process, in which acidic polypeptides generate a liquid-phase mineral precursor, could provide a means for accomplishing this manifold type of crystal control because the precursor phase can be manipulated and shaped into a variety of non-equilibrium crystal morphologies. Our biomimetic approach for the patterned crystallization is based on the combination of the PILP process and Micro-Contact Printing technique, with which we can control the location of film deposition and shape of the growing calcite single crystals. We demonstrate that a liquid-phase mineral precursor is deposited exclusively on specific areas templated with self-assembled monolayers of alkanethiolate on gold, and then the patterned calcitic films grow under constrained conditions via transformation of the PILP phase.
This work is supported by NSF grant BES-9980795.

SESSION HH4: BIOPOLYMERS
Tuesday Morning, November 27, 2001
Independence West (Sheraton)

8:30 AM *HH4.1
MECHANICAL REGULATION OF THE FUNCTIONAL STATES OF PROTEINS. Viola Vogel, David Craig, Wendy Thomas, Andre Krammer, Gretchen Baneyx, Loren Baugh, Department of Bioengineering, University of Washington, Seattle, WA; Klaus Schulten, Beckman Institute, University of Illinois, Urbana, IL.

Intriguing indications are emerging suggesting that mechanical forces may regulate the functional states of proteins by stretching them into non-equilibrium. Using the cell adhesion protein fibronectin as an example, we will discuss molecular design principles, derived from steered molecular dynamics simulations, that nature may employ to tightly control the exposure of fibronectins recognition sites, and/or their relative distances in a force-dependent manner. Fibronectin is an extracellular matrix protein that regulates many cellular functions, including cell adhesion, cell migration and proliferation. Many of these cellular functions are controlled by fibronectin binding to integrins. While integrins have been shown to play a key role in the mechano-transduction of force across the cell membrane by coupling the extracellular matrix to the cytoskeleton, our studies of the fibronectin modules FnIII-9 and FnIII-10, which contain the synergy site and RGD-loop respectively, suggest that fibronectin may be one of the molecules responsible for the initial transformation of mechanical force into a biochemical signal. With the ultimate goal to

proof the computational predictions experimentally, we will show how intramolecular fluorescence resonance energy transfer (FRET) can be utilized to image coexisting conformational states of fibronectin in cell culture.

9:00 AM *HH4.2
MOLECULAR BIOMIMETICS: NANOTECHNOLOGY THROUGH BIOLOGY. Mehmet Sarikaya and A. Jen, *MSE, and F. Baneyx, Chem. E., U. Washington, Seattle, WA; M.L. Snead, Craniofacial Molecular Biology, USC, Los Angeles, CA; K. Schulten, Biophysics, Beckman Center, U. Illinois, Urbana-Champaign, IL; and S. Brown, Molecular Cell Biology, U. Copenhagen, DENMARK.

Structural and compositional control of materials at the molecular scale is a key to the synthesis of novel functional systems. Biological tissues are models for engineering materials as they have excellent combination of physical and chemical properties due to their highly controlled chemical specificity, phase distributions, and morphologies. For example, in all hard tissues (bacterial particles, ordered thin-films, spicules, spines, shells, and dental nanocomposites) in addition to an inorganic component, the common denominator is the presence of polymeric biomacromolecules (proteins and polysaccharides) that may be enzymes, nucleators, habit modifiers, and scaffolds. The biological macromolecules control the intricate architectures from the molecular to macro-level dimensions. One way of developing truly biomimetics material systems for practical technological applications is to engineer proteins for use as molecular erector sets' for self-assembly of hierarchical structures. Using combinatorial biology, we are developing genetic engineering approaches, e.g., cell-surface display and phage display technologies, to select proteins with specific and strong affinity to inorganic surfaces. These genetically-engineered proteins for inorganics (GEPI) have potential significant implications in tailoring surfaces, assembly of ordered and complex nanostructures of metals, functional ceramics, polymers, semiconductors, ferroelectrics and magnetics in applications of nanotechnology, smart materials, bioimplants, drug delivery, tissue engineering, molecular electronics, and nanophotonics.

9:30 AM HH4.3
VISCOELASTIC PROPERTIES OF ENVIRONMENTALLY RESPONSIVE PROTEIN HYDROGELS. Wei Shen, Julia A. Kornfield, David A. Tirrell, California Institute of Technology, Dept of Chemical Engineering, Pasadena, CA; Jill K. Sakata, Univ of Massachusetts, Polymer Science and Engineering Dept, Amherst, MA.

Hydrogels were constructed from triblock artificial proteins consisting of two hydrophobic leucine zipper end-blocks and a hydrophilic random coil midblock. Self-assembly of the leucine zipper domains leads to a reversible transient network, which can be switched on and off by controlling pH and temperature near physiological conditions. The biosynthetic method used to prepare the hydrogels allows engineering of new domains for cell binding and enzymatic recognition, relevant to potential biomedical applications. To achieve rational design for tailorable material properties, viscoelastic properties of these materials were studied systematically as functions of temperature, pH, concentration, ionic strength and molecular structure. We found that the plateau storage modulus is lower than what is calculated based on an ideal network assumption. We believe this is due to the dependence of moduli on the molecular topology. Large fractions of loops and superbridges lower the storage moduli because of a reduced elastically effective chain number density. Formation of loops is favored over bridges when translational entropy gain surpasses conformational entropy loss. So the fraction of loops can be reduced by increasing either the concentration of junction points or the end-to-end distance of the midblock. We are able to show that increasing the contour length or charge density of the midblock, or raising pH to improve solvent quality for the midblock, are effective ways to increase moduli at low concentrations. We also studied the dynamics of these transient networks. Rheological measurements revealed the macroscopic relaxation time, and strand exchange experiments by fluorescence quenching and relaxation techniques yielded the dissociation rate of the leucine zipper domain. By comparing these results, we observed a correlation between macroscopic properties and dynamics on the molecular level. Discrepancies were observed at certain pH values and concentrations, due to the effect of the topology of these transient networks.

9:45 AM HH4.4
ELECTROACTIVE POLYMERIZED VESICLES AS STABLE BIOMATERIALS FOR CHARGE STORAGE SYSTEMS AND ELECTRON COUPLING APPLICATIONS. Ivan Stanish, Alok Singh, Center for Biomolecular Science & Engineering, Naval Research Laboratory, Washington, DC.

Polymerized vesicles, which are submicron, water-dispersible capsules composed of amphiphilic surfactants covalently stabilized into a bilayer ($\sim$ 5 nm) structure, provide for a useful scaffold to immobilize functionally relevant hydrophilic and hydrophobic materials. Our focus is to stabilize and interface vesicle structures composed of bio-derived polymerizable phospholipids and to confer, in a controlled manner, a desired level of vesicle electroactivity. We will discuss design features required to immobilize encapsulated, polymerized vesicles on substrates with a focus on structural stability, conductivity (i.e., electron transport), retention of encapsulated electroactive materials, and surface coverage. In addition, we will discuss potential economic and ecological aspects of polymerized vesicle based-systems that could lead to the development of device with reduced toxicity and decreased processing and disposal costs.

10:30 AM *HH4.5
COMPLEX HIERARCHICAL SELF-ASSEMBLY OF BIOPOLYMERS, MEMBRANES, AND COUNTERIONS.
Gerard C.L. Wong, Materials Science & Engineering Dept., Physics Dept., Bioengineering Dept., University of Illinois at Urbana-Champaign, IL.

This work is concerned a novel class of biomolecular self-assemblies, where new condensed phases of various biopolymers are formed through their interactions with oppositely charged ions of varying complexity, from point-like multivalent ions to charged amphiphilic molecules. Intuitively, two like-charged macromolecules in aqueous solution are expected to repel one another, which is essentially the prediction of prevailing mean-field theories. In the presence of oppositely charged multivalent ions, however, many biopolymers actually attract one another and condense into compact, ordered states. We have examined the global phase behavior of a large range of charged biopolymers: DNA, cytoskeletal F-actin, Fd and M13 viruses. For example, F-actin can form a smart gel with tunable architectures. At low multivalent ionic concentrations, a homogeneous liquid of uncondensed filaments is observed. At high multivalent concentrations, the filaments condense into uniaxial bundles, in the form of close-packed parallel arrays of individual filaments. At intermediate multivalent concentrations, however, we find a new phase of liquid crystalline matter, in the form of a layered stack of multi-axial networks. In contrast, cationic amphiphilic molecules can condense F-actin into hierarchically organized tubules with no direct analog in simple membrane systems. Using high resolution small angle x-ray scattering, confocal microscopy and electron microscopies, we will present a systematic structural investigation of these condensed biopolymer phases, and the resultant implications for new materials.

11:00 AM HH4.6
pH CONTROLLED SELF-ASSEMBLY AND REVERSIBLE COVALENT CAPTURE OF PEPTIDE-AMPHIPHILE NANOFIBERS. Jeffrey D. Hartgerink, Elia Beniash and Samuel I. Stupp, Northwestern University, Dept. of Materials Science & Engineering and Dept. of Chemistry, Evanston, IL.

A series of peptide-amphiphiles have been prepared that are able to self-assemble into discrete nanofibers microns long with a diameter of 7.6nm. The self-assembly process is reversible and can be controlled simply by adjusting the pH of the aqueous environment in which the material is placed. After self-assembly the resultant fibers can be covalently captured through the formation of intermolecular disulfide bonds. These crosslinked fibers are found to have the same dimensions as the supramolecular fibers and are stable to a broad range of pH. The crosslinking process can be reversed by reduction of the disulfide bonds back to free thiol groups giving this system unprecedented flexibility in moving between soluble monomer, self-assembled supramolecular fiber and a high molecular weight, crosslinked polymer. The surface chemistry of these fibers has been designed in such a way to allow them to effectively template the mineralization of hydroxyapatite. The resulting organo-mineral composite has a nanostructure reminiscent to that of bone tissue and may have application in the repair of bone tissues.

11:15 AM HH4.7
NOVEL POLYPEPTIDE-BASED MATERIALS: A BIOMIMETIC APPROACH TO CONTROL STRUCTURE AND FUNCTION OF SYNTHETIC POLYMERIC MATERIALS. Harm-Anton Klok, Max-Planck-Institute for Polymer Research, Mainz, GERMANY.

Proteins are characterized by an enormous structural and functional diversity. Using a limited repertoire of only 20 amino acids, Nature has developed strategies to very precisely control the distribution of these building blocks within a linear polypeptide chain. These linear chains assemble via several hierarchical steps into a three-dimensional architecture, which is largely determined by the peptides primary structure. Applying the concepts Nature uses could allow unprecedented control of structure and function of synthetic polymeric materials. By virtue of their ability to form directed hydrogen bonds, peptides could drive the self-assembly of synthetic polymers into well-defined supramolecular architectures. In addition, the sensitivity of the secondary structure of certain peptides towards

temperature, pH or ion-strength, could allow access to novel stimuli-sensitive materials. In this contribution, two examples of peptide-based hybrid materials will be discussed. In both cases, the supramolecular organization of the materials is determined by the peptide segment and can be manipulated by changing the peptides secondary structure. The investigated materials have a block copolymer type architecture and are prepared by a combination of polymer chemistry and bioorganic (solid phase) synthesis. The first example will discuss the properties of styrene-b-peptide copolymers. In the solid state, these molecules form thermotropic liquid crystalline phases. Unlike most other diblock copolymers, the supramolecular organization of these materials cannot only be changed by varying the length or chemical composition of the constituent blocks, but is also sensitive to temperature-induced conformational transitions. The second example will address poly(ethylene glycol) containing hybrid materials containing peptide sequences derived from natural proteins. In this case, the peptide segments drive the self-assembly in aqueous solution and pH changes can be used to manipulate the self-organization process. The potential of these materials for applications in biomedical technologies will be discussed.

11:30 AM HH4.8
MONOCLONAL ANTIBODY RECOGNITION OF A HISTIDINE-RICH PEPTIDE ENCAPSULATED NANOCLUSTER. Joseph M. Slocik, David W. Wright, Dept of Chemistry, Vanderbilt University, Nashville, TN.

Histidine-rich proteins have been discovered in the digestive vacuole of the human malarial parasite Plasmodium, human blood serum, the vitellaria of the liver fluke Fasciola hepatica, and the fangs of marine polychaetes. In many of these organisms, these proteins have been implicated in the chelation of heme, Cu and/or Zn. For example, the fangs of marine polychaetes containing histidine-rich proteins mineralize with zinc in concentrations of as high as 3% of the metal by dry weight. We have investigated a histidine-rich epitope from HRP II of P. falciparum as a suitable peptide to mediate the nucleation and growth of a number of metal sulfide, metal oxide and zero-valent metal clusters. The clusters have been characterized by UV-vis and fluorescence spectroscopies and transmission electron microscopy. Additionally, the purified nanoclusters have been shown to be immunoreactive with a monoclonal antibody for the specific HRP II epitope.

11:45 AM HH4.9
SELF-ASSEMBLY OF b-SHEET PEPTIDE INTO NANO-HELICAL RIBBON INTERMEDIATES AND NANOFIBERS. Davide Marini[1,2], Shuguang Zhang[2], Wonmuk Hwang[2], Douglas A. Lauffenburger[3] and Roger D. Kamm[1,2,3]. [1]Dept of Mechanical Engr; [2]Ctr for Biomedical Engr; [3]Div of Bioengr and Environmental Health, Massachusetts Institute of Technology, Cambridge, MA.

Short peptides, designed with a repeating sequence of hydrophilic-hydro- phobic amino acids, have been shown to self-assemble into stable, three-dimensional networks of fibers characterized by b-sheet secondary structure. The process by which these molecules coalesce into nanoscale nanofibers and finally produce a hydrogel matrix is poorly understood. Here we report the observation of intermediate structures in the self-assembly of FKE8. The self-organization of FKE8, from individual molecules to nanofibers and nanofiber networks, was followed over time using atomic force microscopy. In the early stages of incubation (minutes) this molecule forms regular nanofibers exhibiting a "helical ribbon" structure with a pitch of ~20 nm and a diameter of ~5 nm. Molecular simulation confirmed the supramolecular structure of these helical ribbons. A combination of numerical simulations and experimental analysis revealed the process of complexity of molecular self-assembly. These findings have significant implications and applications in the molecular design of nanomaterials. Furthermore, these peptide nanofibers share the characteristic features of b-amyloid fibers, thus providing a model system to study amyloid fibers formation and other protein conformational diseases.

SESSION HH5/AA5: JOINT SESSION
BIO- AND SELF-ASSEMBLED ORGANIC-INORGANIC HYBRIDS
Tuesday Afternoon, November 27, 2001
Independence West (Sheraton)

1:30 PM *HH5.1/AA5.1
MULTIPHASE ASSEMBLY AND PROCESSING OF COMPLEX COMPOSITE MATERIALS. Michael Wong, Jennifer Cha, Larken Euliss, Scott Curtin, Eric Chapa, Timothy Deming, Dan Morse Galen Stucky, Dept of Chemistry, Materials Dept and Molecular Biology Dept, University of California, Santa Barbara, CA.

Multiphase media combined with block copolymers, block polypeptides and protein molecules provide a particularly useful synthetic approach to the direct, single system assembly and processing of composite structures with multi-scale structural and functional properties. An added synthesis dimension can be obtained using polymer blends made with combinations such as AB BC or the essentially infinite chi parameter that can be obtained with block copolypeptide or polypeptide - non-ionic polymer linkages. Block copolypeptides and their congeners also provide a convenient route for the incorporation of chirality or cholesteric stereochemistry, and the template use of their secondary structure (beta-pleated sheets or helices) in composite assembly. The processing of block copoly-peptides or polypeptide composite based materials can be carried out with nanoscale extrusion using mesoporous arrays as templates. These combinations can be used to give a large of variety of multicomposition domain configurations. An example is the single step assembly using block copolypeptide polymers with specific binding affinities to metals, metal chalcogenides, metal oxides or organics to arrange nanoparticles of these compositions into well-defined microstructures such that nanoparticles of one composition are spatially oriented in non-aggregated and organized arrays that are completely interior or exterior to nanoparticles or a continuous film of another composition. Some general observations of the multiphase assembly of composite materials will be presented.

2:00 PM *HH5.2/AA5.2
EVOLVING BIOMOLECULAR CONTROL OF SEMI-CONDUCTORS AND MAGNETIC NANOSTRUCTURS. Angela M. Belcher, Chrisitne E. Flynn, Sandra Whaley, Seung-Wuk Lee, The University of Texas at Austin, The Department and Chemistry and Biochemistry, Austin, TX.

Biological systems have a unique ability to control crystal structure, phase, orientation and nanostructural regularity of inorganic materials. We are currently investigating the principles of natural biological molecular recognition in materials and developing new methods to pattern useful non-biological electronic and magnetic materials on new length scales. A peptide combinatorial approach has been employed to identify proteins that select for and specifically bind to inorganic structures such as semiconductor wafers and semi-conductor and magnetic nanoparticles. This approach utilizes the inherent self-organizing, highly selective properties of biologically derived molecules. We are currently investigating peptide recognition and interaction with III-V and II-VI semiconductor materials and magnetic materials. We have selected peptides that can specifically bind to and discriminate zinc-blende III-V semiconductor surfaces. These peptides show crystal face specificity and are being used to organize nanoparticles heterostructures. We have also selected peptides that can nucleate and control particle diameter and aspect ratio of II-VI semiconductor nanoparticles. These peptides are being used to grow nanoparticles and nanowires of specific crystallographic structure and orientation. Using these molecular interactions and specific nanoparticles we are organizing organic/inorganic materials into supramolecular architectures.

2:30 PM HH5.3/AA5.3
PERIODIC POROUS ORGANOSILICAS WITH HEXAGONAL AND CUBIC SYMETRIES : FROM POWDERS TO THIN FILMS. V. Goletto, B. Alonso, F. Babonneau, Chimie de la Matiére Condensée, UPMC, Paris, FRANCE; M. Impéror, P.A. Albouy, Physique des Solides, Université Paris-Sud, Orsay, FRANCE; A.R. Balkenende, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Using surfactant-mediated synthesis, a large variety of organic functions can be incorporated in silica-based nanoporous materials in order to create original materials that can find applications in fields ranging from adsorption, ion exchange, catalysis and sensing technology to nanoelectronics. The organic groups can be easily introduced during the synthesis of the templated network, either as pendant or bridging groups using two families of organoalkoxysilanes, (RSi(OEt)3) and (OEt)-2Si-R-Si(OEt)2 respectively. Various powdered samples have been synthesized introducing alkyl or aryl moieties bonded to Si using methyltriethoxysilane, bis(triethoxysilyl) ethene phenyltriethoxysilane, 1,4-bis(triethoxysilyl)benzene, 1,3-bis(triethoxysilyl)benzene, and 1,3,5-tris(triethoxysilyl)benzene in the presence of cetyltrimethylammonium bromide. Their detailed structural characterization have been performed by means of XRD with synchrotron radiation, one and two-dimensional multinuclear MAS-NMR and adsorption-desorption experiments. Depending on the nature of the precursor and on the experimental conditions (pH, nature of the solvant), 2D-hexagonal (p6m) as well cubic (Pm3n) phases have been obtained, and we have tried to understand the role that the R group could play in the self-asssembly process. Then the synthesis was extended to dip-coated thin films using evaporation induced self-assembly, and once again, we investigated the relationships between the film structures mainly determined by 2-dimensionnal XRD techniques, and chemical parameters.

2:45 PM HH5.4/AA5.4
STRUCTURE CONTROL AND IDENTIFICATION OF INORGANIC-ORGANIC COPOLYMER HYBRIDS. A.C. Finnefrock, G.E.S. Toombes, S.M. Gruner, U. Wiesner, Cornell Univ, Ithaca, NY; R. Ulrich, A. Du Chesne, Max-Planck Institute for Polymer Research, Mainz, GERMANY.

An amphiphilic diblock copolymer, poly(isoprene-b-ethylene oxide) (PI-b-PEO), was used as a structure-directing agent for an inorganic aluminosilicate precursor to generate a variety of highly ordered inorganic-organic nanocomposites. The resulting order and morphology is the consequence of interactions on a hierarchy of length scales, and can be tuned by altering the proportions of the primary constituents. The chemical interaction between the inorganic (IO) component and the ethylene oxide on molecular dimensions leads to a selective swelling of the PEO phase and segregates the three constituents (PI, PEO, IO) into two physical phases (PI, PEO IO) with a length scale of tens of nanometers. This drives the formation of many interesting microstructures (spheres, cylinders, lamella, and ordered continuous structures) with dimensions up to hundreds of nanometers. The ordered continuous structures can be calcined to form mesoporous materials with potential applications in the fields of catalysis, separation technology and microelectronics. The mesoporous microstructures resemble periodic minimal surfaces; discriminating between these similar yet distinct morphologies can be a subtle task. This talk concentrates on the phase identification of the ordered continuous structures using a combination of small-angle x-ray scattering (SAXS), transmission electron microscopy (TEM), and gas adsorption measurements.
A.C. Finnefrock et al., Angewandte Chemie Int. Ed., 40(7):1207-1211 (2001).

3:15 PM *HH5.5/AA5.5
BIO-INSPIRED NANOCOMPOSITES: FROM SYNTHESIS TOWARDS POTENTIAL APPLICATIONS. Tewodros Asefa, Neil Coombs, Hiltrud Grondey, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA; Mietek Jaroniec, Michal Kruk, Department of Chemistry, Kent State University, Kent, OH; Mark J. MacLachlan, Geoffrey A. Ozin, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA.

In recent years, the extraordinary properties of bio-inspired nanocomposites have stimulated great interest in the development of bottom-up synthetic approaches to organic-inorganic hybrid materials in which molecular scale control is exerted over the interface between the organic and inorganic moieties. These developments have led to advanced materials with novel properties and potential use in catalysis, sensing, separations and environmental remediation. Periodic mesoporous organosilica (PMO) materials are an entirely new class of nanocomposites with molecularly integrated organic/inorganic networks, high surface areas and pore volumes, and well ordered and uniform size pores and channels. We have recently extended the approach to include novel single and multi-functional PMO materials that incorporate chiral and heteroatom containing organic functional groups inside the inorganic framework and that may be useful in asymmetric catalysis, enantiomeric separations and heavy metal remediation.

3:45 PM HH5.6/AA5.6
PREDICTING THE MESOPHASES OF COPOLYMER/NANOPARTICLE COMPOSITES. Russell Thompson, Anna Balazs, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; Valeriy Ginzburg, The Dow Chemical Company, Midland, MI; Mark Matsen, University of Reading, Polymer Science Center, Reading, UNITED KINGDOM.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly organized hybrid materials. The morphology of such composites depends on the characteristics of the copolymers and the features of the nanoparticles. To explore this vast parameter space and predict the mesophases of the hybrids, we develop a mean field theory for mixtures of soft, flexible chains and hard spheres. Applied to diblock/nanoparticle mixtures, the theory predicts new ordered phases, where particles and diblocks self-assemble into spatially periodic structures. The method can be applied to other copolymer/particle mixtures and used to design novel composite architectures.

4:00 PM HH5.7/AA5.7
SELF-ASSEMBLY MECHANISMS INVOLVED IN THE FORMATION OF SiO_2, TiO_2, Al_2O_3, ZrO_2 AND V_2O_5 MESO-STRUCTURED HYBRID FILMS AS REVEALED BY IN-SITU SAXS ANALYSIS. David Grosso, Galo J. de A.A. Soler-Illia, Eduardo Crepaldi, Ludivine Pidol, Florence Babonneau, Clément Sanchez, LCMC-UPMC, Paris, FRANCE; Pierre-Antoine Albouy, LPS, Université Paris-Sud, FRANCE; H. Amenitsch, Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Graz, AUSTRIA.

The formation of meso-structured materials, involving the polycondensation of inorganic precursors in solution combined with the structuring effect of surfactant mesophases, is a complex process that is governed by the interactions existing at different levels into such multiphases systems. However, this method has proven to be relatively robust and reproducible as long as the critical parameters can be controlled. The preparation of meso-structured thin films by liquid deposition techniques is further complicated by other parameters which are the liquid phase evaporation, the presence of film/air and film/substrate interfaces and the capillary and shearing forces existing at these interfaces. In this work, we studied the auto-assembly mechanisms taking place during dip-coating of SiO_2, TiO_2, Al_2O_3, ZrO_2 and V_2O_5 templated films exhibiting the p6m 2D-hexagonal structure. Initial solutions were composed of aqueous ethanol solvent in which was dissolved the inorganic precursors and the Brij 58 copolymer structuring agent. If needed, the pH was adjusted by adding hydrochloric acid or ammonium hydroxide. The time-resolved structural formation and evolution of the meso-organization in such thin films was followed by in-situ SAXS through synchrotron radiation. The film thickness profile associated to the advancement of the liquid phase evaporation was simultaneously observed via in-situ interferometry. The self-assembly model deduced from these experiments shows that different type of interactions force the system to evolve at different stages of the drying process, and that the presence of both film/air and film/substrate interfaces play a key role in the orientation of the organized domains.

4:15 PM HH5.8/AA5.8
IN-SITU X-RAY SCATTERING STUDIES DURING EVAPORATION INDUCED SELF-ASSEMBLY OF SILICA-SURFACTANT NANOSTRUCTURES/MESOPHASES. Dhaval A. Doshi, Nanguo Liu, Hongji Chen, Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM; Valerie Goletto, University of Paris, Paris, FRANCE; Darren Dunphy, Scott Reed, Sandia National Laboratories, Albuquerque, NM; Andrew MacPhee, Suresh Narayananan, Jin Wang, Advanced Photon Source, Argonne National Laboratories, IL; Benjamin Ocko, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; Alan Hurd, Los Alamos National Laboratory, Los Alamos, NM; Alain Gibaud, University of Maine, LeMans, FRANCE and Sandia National Laboratories, Albuquerque, NM; C. Jeffrey Brinker, Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, University of New Mexico and Sandia National Laboratories, Albuquerque, NM.

Structure formation via amphiphilic molecules such as lipids is ubiquitious in nature. From the cell membrane to detergent soap bubbles their uses are endless. Kresge and co-workers used surfactants to organize inorganic materials such as silica. Since then various amphiphilic molecules such as lipids, surfactants, block co-polymers have been used to self-assemble a wide spectrum of silica nanostructures. Although such materials have been extensively studied in their final form, very little is known about their formation mechanism. We have conducted in-situ x-ray scattering studies to elucidate the co-operative self-assembly process. Starting from a homogeneous solution of silica, ethanol, water, acid and surfactant solvent evaporation enriches the system in surfactant thereby fostering the self-assembly of the silica-surfactant mesophases. Following such an evaporation process in-situ with x-rays allows us to observe various stages of self-assembly from micellization to mesophase formation. Results from experiments conducted at the synchrotron facilities of Brookhaven national laboratory and Argonne national laboratories will be presented.

4:30 PM HH5.9/AA5.9
NANOFABRICATION OF INORGANIC MATERIALS USING CATIONIC LIPID-BIOPOLYMER SELF-ASSEMBLED SYSTEMS. Hongjun Liang, Thomas E. Angelini, James Ho, Paul V. Braun, Gerard C. L. Wong, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL.

It has been shown that cationic lipid-DNA complexes can self-assemble into a nanoporous lamellar structure, in which 1-D ordered DNA arrays are intercalated between planar lipid membrane sheets. The DNA spacings can be tuned from 2.5nm to 6.0nm, and essentially define an array of pores with tunable sizes. These DNA membrane complexes and other related self-assembled systems can be used as templates for the synthesis of nanostructured inorganic materials, such as quantum dots or quantum wires. Charged metal cations can be confined in the biomolecular self-assemblies described above and subsequently crosslinked. In this work, we employ cationic

lipid-DNA complexes to control the formation of CdS and related compounds, by variation of parameters such as the membrane charge density, the relative DNA-lipid membrane stoichiometry, and the number of condensed metal ions. We have characterized these composite self-assembled phases of DNA, membrane lipids, and metal cations (both before and after crosslinking) in a series of detailed Small Angle X-ray Scattering (SAXS) and optical microscopy experiments. In addition, we have developed a number of new methods that quantitatively measure the density of condensed metal ions in such complexes. Preliminary results on the morphologies of the templated phases as a function of these parameters will be presented.

4:45 PM HH5.10/AA5.10
PHOTOCHEMICAL PATTERN TRANSFER, ENHANCEMENT, AND RECOGNITION IN THIN FILM SILICA MESOPHASES. A.M. Dattelbaum, Laurel Ecke, Robert A. Provencal, Andrew P. Shreve, Atul N. Parikh, Bioscience Division, Los Alamos National Laboratory and Department of Applied Science, University of California, Davis, CA.

We have recently shown that a nominally room temperature photochemical method, simply employing ultraviolet light (187-254 nm) generated ozone environment, provides an efficient method for the removal of surfactant templates for a routine production of well-ordered, mesoporous silica thin films at low temperatures. The treatment concomitantly strengthens the silicate phase by fostering the condensation of unreacted silanols leading to mesoporous thin films with well-defined mesoscopic morphologies. Here, we show that this photochemical "calcination" process lends itself for convenient removal of surfactants in laterally defined regions at micrometer length scales and above allowing for photochemical pattern transfer. We further show that the selective functionalization of exposed regions using etching (HF), surface self-assembly (monolayer and bilayer depositions), and condensation (e.g., by water) leads to significant pattern enhancement and pattern recognition. Potential uses of patterned mesoporous thin films will also be discussed.

SESSION HH6: SURFACES AND INTERFACES
Wednesday Morning, November 28, 2001
Independence West (Sheraton)

8:30 AM *HH6.1
HARNESSING THE ENGINES OF LIFE: THE ART AND SCIENCE OF ENGINEERING HYBRID NANOFABRICATED MECHANICAL DEVICES. Carlo Montemagno, University of California-Los Angeles, CA.

Scientists and engineers have anticipated the potential benefits of integrating engineered devices to living systems at the molecular level for many years. Such devices offer the potential of taking advantage of the best attributes associated with both worlds. Hybrid living/non-living systems can potentially possess many of the essential properties of life such as the abilities to "intelligently" self-assemble, repair, and evolve. We will present the results of our efforts to incorporate biological energy transduction processes and cell signaling pathways into engineered nanofabricated devices. In particular, we will illustrate our strategy for fueling, controlling and integrating a recombinant, thermostable F1-ATPase biomolecular motor with a NEMS to create an engineered hybrid device.
Included in the presentation will be the initial results of our efforts to develop and demonstrate an integrated F1-ATPase powered NEMS device that is fueled by light-driven ATP production. ATP is synthesized from light using artificial liposomes (ca. ~150 nm in diameter) comprised of reconstituted FoF1-ATP synthase and bacteriorhodopsin. Subsequently, the ATP is used to provide energy to power a recombinant, thermostable F1-ATPase biomolecular motor (ca. ~12 nm) that is coupled to a NEMS device. Our current analysis indicates that a light collection area as small as 500 nm^2 will provide enough energy to power each F1-ATPase biomolecular motor. A single F1-ATPase biomolecular motor can generate a torque consistent with the force required to move engineered nanomechanical structures. We will also present our technique for integrating nanomechanical structures to biomolecular motors with a precision ~ 40 nm. Scientists and engineers have envied the elegance of molecular level energy transduction in living systems for many years. This work capitalizes on a core feature of living systems, the capability of transforming diverse sources of energy into a generic energy currency that can be universally used. The integration of a synthetic photosynthetic system with NEMS establishes a new mechanism for fueling the next generation of nanoelectromechanical devices. Light is used to produce ATP from ADP and P, the ATP is used by the F1-ATPase biomolecular motor to produce work with ADP and P as waste products. Ultimately, we anticipate that this chemically closed system will be used to pump fluids, open and close valves in microfluidic devices, provide locomotion, and possibly generate electricity. The potential applications for sub-micron size, light powered, autonomous devices or "Smart Dust" are many including long-lived microscopic intelligence and environmental sensors.

9:00 AM *HH6.2
ENGINEERING POLYMER SURFACES: DEALING WITH COMPLEXITY. Christopher K. Ober, Xuefa Li, Seok-Ho Kang, Cornell University, Dept of MS&E, Ithaca, NY; Edward J. Kramer, Alex Hexemer, Easan Sivaniah, University of California at Santa Barbara, Dept of Materials, Santa Barbara, CA.

Biological materials are complex systems that derive their structure from the interplay of many small-scale forces. While difficult to duplicate in synthetic materials, a number of self-assembling processes can be incorporated into polymers. As an example of where such an approach might be useful, there has been much interest in creating polymer surfaces that resist biological fouling. Self-assembly can be a powerful tool for tailoring surface properties because it enables the creation of stable surfaces. Nevertheless, the best strategy for accomplishing this is not clear. Both extremely non-polar and very hydrophilic surfaces have been examined and to some extent both strategies work. To better understand issues associated with the biofouling process, surface active block copolymers (SABC) were prepared with either non-polar semifluorinated groups or hydrophilic poly(ethylene glycol), PEG, side groups were attached to hydroxylated poly(styrene-b-1,2/3,4-isoprene). Their surface properties have been examined using a variety of methods including contact angle measurements, atomic force microscopy and near edge X-ray absorption fine structure (NEXAFS) studies. Preliminary investigations of cell binding and protein adsorption have also been carried out. We will describe the synthesis of these materials, report the surface behavior of these new surface-active block copolymers and report on the relative success of these strategies. Acknowledgements: Support of the Office of Naval Research, the National Science Foundation-Division of Materials Research and the use of the U7A beamline at Brookhaven National Laboratories are appreciated

9:30 AM HH6.3
BIOMIMETIC WATER-REPELLENT SURFACES PREPARED BY USING MICROSTRUCTURES OF PHASE-SEPARATED POLYMER MIXTURES. Osamu Takai, Jun Iwai, Yasushi Inoue, Hiroyuki Sugimura, Department of Materials Processing Engineering, Nagoya University, Nagoya, JAPAN.

Leaves of lotus show ultra or super water-repellency, a phenomenon where a solid surface shows the contact angle for a water drop of more than about 150 degrees, because of the precisely controlled roughness of their surfaces. Recently we have synthesized ultra water-repellent silicon oxide films by plasma-enhanced CVD (PECVD) using organosilicon compounds as row materials. These film surfaces are biomimetic surfaces of the leaves of lotus. In the CVD process, we achieved simultaneously both the roughness and the hydrophobic character on the surface by depositing nano-size clusters of the reactant molecules polymerized in the plasma. In this study, we have developed a new method to prepare water-repellent surfaces based on the nanoporous structure of a spin-coated layer of phase-separated polymer mixtures covered with a hydrophobic thin layer. We fabricated the polymer layer with the nanoporous structure on glass substrates by dissolving one of the phases in the spin-coated polymer mixtures of polymethylmethacrylate (PMMA) and polystyrene (PS). The hydrophobic layer was deposited by PECVD using tetramethylsilane (TMS) as a reactant. Surface morphology, water wettability and chemical bonding states of the films were characterized by using AFM, a static contact angle meter and FTIR. An environmental scanning electron microscope (ESEM) was used to observe the appearance of micro water drops on the surfaces. AFM observations show that the nanoporous structure of PMMA after dissolving the PS phase was varied with the preparation conditions, the repetition number of spin-coating, the molecular weights and also the mixture ratio of the polymer materials. Optimizing these conditions, we obtained a water contact angle of 120 degrees. After the deposition of the hydrophobic layer, the water repellency was improved up to 135 degrees. ESEM observations show that the contact angle is locally much higher than the macroscopic value. This work is supported by JSPS-RFTF99R13101.

9:45 AM HH6.4
RAPID, SENSITIVE, SELECTIVE BIOSENSOR USING A SQUID MICROSCOPE. Helene Grossman, Yann Chemla, Yan Poon, Richard Bruehl, Carolyn Bertozzi, Raymond Stevens, John Clarke, and Mark Alper, Departments of Physics, Chemistry and Molecular and Cell Biology, University of California at Berkeley, and Division of Materials Sciences, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA.

A fast and versatile technique has been developed for selective detection of very small quantities of molecules or microorganisms. It

is based on the detection of magnetic signals by an ultrasensitive "microscope" based on a high-transition temperature Superconducting QUantum Interference Device (SQUID). A sample suspected of containing the target is placed in the well of the microscope which has been coated with antibodies against the target. A solution containing nanometer-size magnetite particles bound to target-specific antibodies is also placed in the well. A pulsed magnetic field aligns the dipole moments of the particles, and the SQUID measures the magnetic relaxation signal when the field is turned off. Unbound magnetic particles relax rapidly (microseconds) by Brownian rotation and are not detected. On the other hand, the signal from immobilized particles bound to targets slowly relax by the Neel mechanism over a few seconds. As a result, only bound particles contribute to the signal, allowing for quantification of the number of targets present without the need for a wash step. The current system requires no more than 30,000 immobilized magnetic particles for a measurable, reproducible signal, a sensitivity greater than that of the commonly used Enzyme-Linked Immunosorbent Assay (ELISA). A new SQUID microscope has been designed and built, which may improve the sensitivity by up to two orders of magnitude, thereby allowing detection of as few as 500-1000 particles. The number of target molecules that can be detected will be fewer, depending on how many magnetic particles bind to each target.
Supported by U.S. DOE Contract DE-AC03-76SF00098

10:15 AM *HH6.5
NEW RESULTS ON ACTIVE MEMBRANES. P. Girard[1], I. Derenyi[1], F. Julicher[1], S. Ramaswamy[3], A. Roux[2], G. Cappello[1], P. Bassereau[1], B. Goud[2], J. Prost, [1]Curie Institute, Section de recherche, Paris, FRANCE. [2]Curie Institute, Section de recherche, Paris, FRANCE. [3]Indian Institute of Science, Phys Dept, Bangalore, INDIA.

I will describe recent advances both at a theoretical and an experimental level concerning membranes maintained out of equilibrium either by the action of pumps or of kinesins moving on microtubules.

10:45 AM *HH6.6
REGULATING CELL-SURFACE INTERACTIONS WITH AMPHIPHILIC COMB POLYMERS. Anne M. Mayes, Darrell J. Irvine, Dept of Materials Science and Engineering, MIT, Cambridge, MA; Linda G. Griffith, Dept of Chemical Engineering and Div of Bioengineering and Environmental Health, MIT, Cambridge, MA.

The objective of our research is to develop facile methods for fabricating biomaterial surfaces that regulate cell response by simultaneously eliminating nonspecific protein adsorption and presenting a controlled spatial distribution of peptide ligands to elicit receptor-mediated cell response. The agent of surface property modification in this work is an amphiphilic comb polymer designed to provide a hydrated PEG brush-like surface structure that effectively resists protein adsorption and introduces mobile, end-tethered peptide signals (e.g., RGD or EGF) that can interact efficiently with cell receptors. Combined theoretical and experimental studies indicate that the amphiphilic comb polymers self-organize at water interfaces, adopting a quasi-2D backbone conformation that allows for clean regulation of the spatial presentation of nanoscale clusters of surface-bound adhesion peptides. Cell adhesion assays comparing combs with ~5, 3, and 1 tethered RGD groups indicate significant clustering effects on adhesion strength for equivalent average peptide surface coverage. The self-organizing properties of these molecules can be further exploited in various fabrication schemes to achieve control of the spatial density and distribution of ligands on the surface over 4 orders of magnitude (10 nm - 10 microns).

11:15 AM HH6.7
ENGINEERING DNA-BASED SURFACES FOR DIRECTING ASSEMBLY. Paul Laibinis, Ivan Lee, Manish Bajaj, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

We have developed methods for generating surfaces expressing covalently grafted, end-immobilized oligonucleotides with sequence lengths of hundreds of base units. These surfaces provide a modular platform for directing tailored building blocks into selected organized forms. The oligonucleotides are immobilized using DNA base pairing as a motif for organizing these structures at a surface. Specifically, chemical synthesis of shorter length oligonucleotides is used to present surfaces that are then subsequently derivatized. The surface density of these first oligonucleotides (typically, eight to ten base units in length) is controlled using alkylsiloxane monolayers that expose both reactive hydroxyl groups and inert methyl groups. Control over surface composition and sequence affords an ability to maximize the hybridization activity of these strands. X-ray photoelectron spectroscopy provided a convenient approach for assessing surface coverages and reaction yields in preparing these strands. Hybridization experiments clearly indicated that oligonucleotide coupling efficiency increased with decreasing oligonucleotide surface density, and also with increased coupling time. Hybridization efficiency was inversely related to oligo surface density, and optimal hybridization yield was achieved at an oligonucleotide surface density of between 3 and 5 x 10^{-11} moles/cm^2. dsDNA strands were successfully hybridized to these surfaces with surface densities of approximately 2 x 10^{-12} moles/cm^2. Psoralen crosslinking to hybridized strands was observed to proceed at efficiencies of 30-50% to generate end-immobilized, covalently grafted DNA strands that allowed sequence lengths of hundreds of base units to be probed in subsequent hybridization experiments. The general strategy provide a powerful method for directing assembly onto surfaces and thereby for organizing the component species of a material.

11:30 AM HH6.8
FABRICATION OF PHOSPHOLIPID BILAYERS IMMOBILIZED ONTO SOLID SUPPORT. Ivo Doudevski, Junqi Ding, Heidi Warriner, Joseph Zasadzinski, University of California, Dept of Chemical Engineering, Santa Barbara, CA.

In this report we outline our investigations on the effect of albumin on model lung surfactants using phospholipid bilayers. Lung surfactants line the air-water interface in the lungs of air-breathing mammals, substantially reducing the surface tension at air-water interface and therefore the work of breathing. Phospholipid bilayers immobilized onto solid support represent a suitable model to mimic in vitro the behavior of phospholipid lung surfactant mixtures upon exposure to serum proteins such as albumin. We report two alternative techniques for fabrication of phospholipid bilayers immobilized onto solid support. As a model lung surfactant we use a mixture of dipalmitoylphosphatidylcholine (DPPC), 1-palmitoyl-2-oleoyl-phosphatidylglycerol (POPG), palmitic acid (PA), and a mutant surfactant-specific protein (SP-B1-25). Using a home-designed Langmuir trough equipped with fluorescent microscope, we simulated lung surfactant phase behavior at the air-water interface. We then combined reverse and standard Langmuir-Schaefer deposition techniques in order to produce an immobilized phospholipid bilayer on the mica surface. Alternatively, we employed a new technique for deposition of the second phospholipid layer in which the mica substrate covered with a phospholipid monolayer was brought in contact with a phospholipid monolayer at the air-water interface. Upon contact with the substrate the second phospholipid layer was immobilized on the top of the first one and was then pulled off the air-water interface. We performed atomic force microscope (AFM) observations of the phospholipid bilayer. The film was then exposed to 2 mg/mL albumin solution in buffer. AFM observations showed significant morphological changes of the phospholipid film as a result of exposure to albumin solution. This observation compares favorably with other reports suggesting that the lung surfactant physiological function was hampered in presence of sufficiently concentrated albumin.

11:45 AM HH6.9
DNA-DIRECTED ASSEMBLY OF METAL PARTICLES. Christine Keating, Brian Reiss, Sheila Nicewarner, Penn State Univ, Dept of Chemistry, University Park, PA.

This presentation will focus on the use of deoxyribonucleic acid (DNA) to direct the assembly of metal particles, and the impact of polymeric solutes on the temperature-dependence of this process. DNA has been attached to the surfaces of colloidal Au spheres as well as metal nanowires several microns in length, and the ability of this particle-bound DNA to selectively and reversibly bind complementary sequences has been verified. When complementary sequences are located on two different metal surfaces, hybridization can be used to direct the assembly of particles in solution or onto macroscopic surfaces. Inspired by the impact of macromolecular crowding, or volume exclusion, upon cellular assembly processes, we have investigated the effect of several polymeric solutes upon the DNA-directed assembly of metal particles. The directed assembly of metal particles can be exploited either for bioanalysis or for materials synthesis. For example, the assembly process can report on the presence of a DNA sequence of interest, with particles acting as amplification tags to facilitate detection. A second application of DNA-directed assembly is in the deterministic construction of nanostructured materials. We are particularly interested in the potential of DNA hybridization to selectively connect metal nanowires into functional electronic devices. To this end, we are investigating DNA assembly and hybridization on nanowires, and the construction of very simple DNA-linked structures. It is possible to selectively derivatize Au and Pt surfaces; this chemistry has been used to immobilize DNA on only the central segments of Pt-Au-Pt striped nanowires. Simple crossed nanowire structures have been prepared in solution based on this chemistry; optimization of this process will be discussed.