SYMPOSIUM HH
Bio-Inspired Materials—Moving Towards Complexity

November 26 – 28, 2001

Chairs

Bradley F. Chmelka
Dept of Chemical Engr
Univ of California-Santa Barbara
Engineering II Bldg Rm 3336
Santa Barbara, CA 93106-5080
805-893-3673

Konrad Knoll
BASF AG Ludwigshafen Germany
Ludwigshafen, D-67056 GERMANY
49-621-6021393

Joachim P. Spatz
Organische Chemie III
Ulm Univ
OC3 Makromolekulare Chemie
Ulm, D-89069 GERMANY
49-731-5023862

Ulrich B. Weisner
Dept of M$\&$E
Cornell Univ
329 Bard Hall
Ithaca, NY 14853-1501
607-255-3487

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A Joint Proceedings with Symposium FF/GG/HH
to be published in both book form and online
(see ONLINE PUBLICATIONS at www.mrs.org)
as Volume 711
of the Materials Research Society
Symposium Proceedings Series

*Invited paper
SESSION III: BIOMINERALIZATION
Monday Morning, November 26, 2001
Independence West (Sheraton)

8:30 AM *III.1
CONTROL OF THE SHAPE AND STRUCTURE OF CALCIUM CARBONATE MINERALS BY ORGANISMS. Yosi Levi-Kalisman, Sedi Raz, Boaz Barnea, Ingmar Wieland, and Lior Addadi. Weizmann Institute of Science, Dept. of Structural Biology, Rehovot, ISRAEL.

Organisms produce mineral-reinforced composite materials for different purposes. Each has a unique, 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 electronic structure that is compatible 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 bilamellar sponge and meduses are composed of amorphous calcium carbonate (ACC). The same material is deposited in the first layer of the shallow shells of some molusks. It also strengthens the corallite of the corals and is deposited in the leaves of plants in the form of xyloliths. The stabilization of the unstable ACC requires introducing into the hydrated phase macromolecules and other additives during deposition. Although all the above minerals have selectively 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 is, by the transformation of a controlled manner. The resulting single crystal assumes the shape of the initial phase. Some urchins have adopted this solution in their shallow spines. Finally, mollusk shell marine consists of polycrystalline aragonite formed inside a matrix composed of calcium carbonate, possibly the most common in nature. We have proposed that the matrix consists of a layer of thin scaffold swollen with a significant fraction of a calcium carbonate, the latter then crystallizes into aragonite under the control of an assemblage of acid macromolecules.

9:00 AM *III.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 remind us of those produced by biology, a possible outcome of the current nanotechnology era. In biology we see the self-assembly of proteins and polysaccharides producing remarkable soft materials such as skin, 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 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 independently controlled fashion. Such materials may turn out to be useful in nanotechnology or nanomedicine. In this last application their role could be to carry signals or important cargo to cells. To make these materials reconstitute or be released. In our laboratory we have designed recently peptide amphiphiles with the capacity to self-assemble reversibly and in high aspect ratio nanoparticles that mimic collagen in extracellular matrices. The molecule construct allows the multiplexing of signals to receptors on cells, and also the formation of ionic crystals oriented relative to the nanofibers in a way that mimics the nanostructure of bone.

9:30 AM *III.3
PIECE-BY-PIECE STRUCTURE DETERMINATION OF SEQUENCE MODULES FOUND IN THE ELASTOMERIC BLOOMINERAL-ASSOCIATED PROTEIN, LUSTRIN A: WHAT HAVE WE LEARNED? Brandon Winston, Bo Zhang, Kuo Zhou, Daniel Morse, and John Spence. Enzyme 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 whole molecule is a primary amino acid sequence, a translation of the evolution, the protein has acquired several multifunctional domains: A) Eight pro-rich domains (Polomains); B) Ten, O-step homologs that are rich in Gly, Ser, or Tyr; C) 28-residue Arg, Lys, Tyr-rich domain; (D) 24 residue Asp-containing triplet region. As shown in previous studies, the Lustrin A plays a crucial role in abalone shell formation and maintenance 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 this domain may modulate some role of more of these functions. We have embarked on NMR and MALDI hydrogen/deuterium structural studies on several sequence regions of Lustrin A: (A) the NPNN consensus repeat found in the terminal domains of the C-domains; (B) the basic 38 residue Arg, Lys, Tyr-rich domain; and (C) the 24-residue Asp-containing triplet region of the CT terminal domain. These studies have complemented the work of other laboratories. The N-terminal domain of the C-domain has not been identified by electron microscopy, X-ray crystallography or CD spectroscopy.

9:45 AM *III.4
BIOINERT MINERALIZATION IN ENGINEERED VIRAL PROTEIN CAGES. Trevor Doughty, Erica Strible, Temple University, Dept. of Chemistry, Philadelphia, PA; Mark Young, Debbie Willetts, Montana State Univ, Dept of Plant Sciences, Bozeman, MT; Matthew Liborn, Adelphia Institute, Stevens Institute of Tech, Dept of Chemical, Biochemical and Materials Eng, Hoboken, NJ.

The coat protein of the cowpox variola virus (CCMV) has been genetically engineered to act as a mimic of organic mineralization 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 an algorithmic electrostatic interactions present on the exterior 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 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 *III.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 extends present human capabilities, biological systems fabricate hierarchically organized mineral-polymer composites at low temperatures and neutral pH. Analysis of the proteins, genes and molecular mechanisms governing the formation of such composites in abalone shell and sponge bone reveal that the origin of both the exquisite nanostructural control and the extraordinary high-performance capabilities of these biomaterials is 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, unexpected new discoveries of self-assembling molecular structures, 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, are leading the development of new low-temperature biomimetic routes to the synthesis of advanced mineral-organic composites.

11:00 AM *III.6
MODEL-BASED BIOMIMETIC NANOCOMPOSITE DESIGN.
We have developed a multiscale modeling approach that predicts mechanical responses of nacre, mother-of-pearl, incorporating experimentally-determined nacre properties into mesoscopic 3D numerical analysis. Nacre is a laminated, segmented, hybrid nanocomposite consisting of 10-20% organic matrix that surrounds 250 nm-thick CaCO₃ pseudo-hexagonal platelets that are staggered across layers, a brick-mortar nanorachitectural. 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., clams, bivalves, and gastropods, have nacre structure that has survived millions of years of evolution. Our model incorporates defects of nanoscale 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 nanindentation 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 adhesives and chemical compatibility. Our model may have significant implications for simulating the self-assembly of layered hybrid nanostructures for practical engineering applications as wear resistant, impact resistant, tough, and durable materials.

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

We have synthesized poly(ethylene glycol)/poly(l-lysine) block copolymers (PEG/PLA) possessing an aldehyde group at the PEG chain end and a pyrene molecule at the PLA chain end, which forms coil-type block copolymers possessing planar bilayer-like nanostructures 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 localization of the pyrene molecules in the very limited core space. The aldehyde groups on the micelle surface were converted to biotin moieties using biotin 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 follows: due to the suppression of the mobility of the PEG chain end by the interaction with avidin, the stability of the self-assembly structure of the particle decreased to result in collapse or loosen the assembled structure, which causes decrease in the excimer emission drastically. This exciting monitoring system is anticipated for new molecular recognition systems.

SESSION HH2: BIOMINSPIRED SYNTHESIS AND PROPERTIES
Monday Afternoon, November 26, 2001 Independence West (Sherron)

1:30 PM HH2.1 FUNCTIONAL SURFACE STRUCTURES VIA SELF-ASSEMBLY OF BLOCK COPOLYMERS, Martin Mueller, Christoph Hortmann, Silke Heidtmueller, Verena ZH. Chan, JoachimP. Spatz, H.G. Borchardt, P. Ziemann, University of Ulm, Laboratory of Organic and Macromolecular Chemistry, OC III. Laboratory of Solid State Physics, Ulm, GERMANY.

Arrays of nanometer sized metal and metal oxide particles are generated by means of a polymer template. In the first place polymer 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 35 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 cell in an ordered array and for patterned SAMs. Formation and compartmentalization of metallic nanodots within block copolymer micelles can be combined with a step down approach, i.e. electron beam lithography. The combination pushes the limit of standard lithography to nanometer patterned Si without special and very expensive equipment. Within a core prestructure, > 30nm, 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 a few nanometers can be arranged in lines and as individual dots in periodic as well as in aperiodic patterns separated by micrometers. Soldering of linear arranged gold dots can lead to the fabrication of...
Proteins of virus capsids self-assemble in the form of regular hollow icosaedra. These also appear as a result of biomineralization, but are extremely rare in mineral crystals. However, self-assembled aggregates of icosaedrual shape made of synthetic organic components such as surfactants has never been reported. We describe here self-assembled bilayer organization in the form of hollow aggregates of regular icosaedrual shape formed at concentrations in salt-free mixtures ofionic and cationic surfactants (bicarbonate). The aggregates are composed of pores located at the vertices which are about one micron apart. The size (about 1μm) and mass (about 1010 Da) of the aggregates larger than any known icosaedral protein or virus capsid. The wall rigidity is in the range of 10 kN/m (analogous to cardiolipin bilayers) and is due to the strong unscreened electrostatic interaction between the two oppositely charged surfactants whose hydrocarbon chains are crystallized. Electron microscopy, light, X-ray, and neutron scattering results demonstrating the stability (in the complete absence of salt) of faceted 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, ENCAPSED LC'S, AND RELATED BLOCK POLYMER AGGREGATES. Harry Bermudez, Baldomar Diezdero, Paul Dahlenberg, 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 'polysome' membranes. Free radical polymerization was used subsequent to self-assembly of PEOPolybutadiene vesicles. We describe a series of such dials 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 1500 Atm - orders of magnitude greater than any natural liquid membrane - are consistent with strong tethering between close-packed neighbors. The enormous ability of the giant vesicles can be tuned down for application; blending in the hydrophobic analog polyethyleneoxide-polybutadiene produces vesicles that are stable, as well as the rupture strength by orders of magnitude. Results are consistent with rigidity permeation through a finite-layer stack of two-dimensional lattices. Moreover, below the percolation limit, a regime of supratranslational motion exists, reflecting perhaps nanoscopic demixing and suggestive of the limitations encountered with low reactivity lipids. The results with membranes provide general insights into coeval crosslinking within self-assembled nonmacromolecules. Liquid crystals, among other compounds, have been encapsulated in these vesicles and manipulated with the aim of understanding pseudocylindrical dynamics of micro-encapsulated complex media. Emerging work on rod mixtures should provide new opportunities for pseudocylindrical structuring of our synthetic cell membranes.

4:25 PM HH2.4 OPTICAL PROPERTIES OF SELF-ASSEMBLED CYLINDRICAL LIGHT-HARVESTING SYSTEMS. Jasper Knoester, Marika Bednarek, Koco Dugaan, Stefanin Lampropoulou, Univer Groningen,

Materials Science Center, Groningen, THE NETHERLANDS; Siegfried Diederich, Christian Spitz, Andre Oertl, 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 complexes, 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 dichroism of the assembly of lipids (LH2) and bilayers 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 exciton 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 in 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 femtosecond 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 BIPYRIDINE-ENCODED MACROMOLECULES. C.D. Eisenbach, J.L. Kensten, K. Dimberger, 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 biological systems. This has been investigated for the copper(I) complex formation of 6,6'-disubstituted oligo(2,9-bipyridinyl) (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(bpy)2]PEO diblock copolymers exhibited a recognition-induced and direction-controlled self-assembly upon complexation with Cu(I) ions resulting in well-defined dimers. The double-helical polymer complex of the diblock copolymer dimers formed a microphase-separated system with ordered domains of the bpy/Cu(I) complex blocks. The implications for the bipy 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 Demf, Institut Louis Langeron, Grenoble, FRANCE; Monique Dubois, Thomas Zemb, Service de Chimie Moléculaire, CEA-Saclay, Gif sur Yvette Cedex, FRANCE; Thaddée Gilik-Krzywinski, 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 shorter than the bilayer thickness, are extremely scarce in literature. The reason for that is bilayers including a thick (~3 nm) layer of molten hydrocarbon chains, covered by a large structural charge (1 charge 5.0 nm) are expected to be off. These stiff bilayers are expected to be too thick, hence producing sharp Bragg peaks. We used DOP as model system of charged bilayers in the [Lustre] state. Samples are birefringent, electron microscopy shows bilayer stacks, but the Bragg peaks in the X-ray scattering show only twin-like SAXS and SAED patterns show a peculiar behaviour: in a certain range of (controlled) anionic 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 VEHICLE SIZE, PHASE BEHAVIOR AND STABILITY OF LARGE UNILAMINAR VESICLES. Leila Fraugger, Geoffrey Stracke, 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 diphenyl 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-dipalmityl-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 or at a concentration of 100 mol% for 2 hours. In contrast, about 20% of the total was released from the liposomes in the absence of Pluronic P85. The data clearly demonstrate that the ASMs interact strongly with lipid bilayers without disrupting the membrane, which is in contrast to the actions of Pluronic P85.

4:30 P MHH2.8
PROTEIN-NANOPARTICLE CONJUGATES: STRUCTURE AND OPTICAL PROPERTIES. FOR ADVANCED MATERIALS IN ELECTRONICS AND MEDICINE. Nataliya N. Manokhina, 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 galvitic dithioacetylated 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. General 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 emission enhancement in the cryptophan 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 P MH2.9
ENZYMATIC CONTROL OF OLIGONUCLEOTIDE-NANOCRYSTAL CONJUGATES. C. Steven Yin and Geoffrey F. Stroeve, University of California, Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

The two- and three-dimensional assembly of metallic and semi-conducting nanocrystals, such as CdSe and gold, using both biological and organic oligomers hold potential as archetypal structure for nano-electronics as well as biological sensors. The employment of DNA manipulation at the atomic level 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 methyltransferase enzymes will be shown.

SESSION HH2: POSTER SESSION
BIOMIMETIC MATERIALS: MOVING TOWARDS COMPLEXITY
Monday Evening, November 26, 2001
8:00 PM
Exhibition Hall D (Hynes)

HH2.1
COLLAPSED HYDROGEL MAY FIND ITS FACULTY. Yasuo Takeoku, 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 weak interactions between polymer chains and showed thermo-sensitive volume change in water. The diameter of the gels at high temperature, where the gel collapsed, is 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 catalyse a chemical reaction but also switch their catalytic on and off response to an infinitesimal change in solvent composition. The gel consists of two species of monomers. The major component, N-acryloxyphosphamide, makes the gel swell and shrink in response to a change in composition of ethanol/water mixtures. The minor component, vinyl-maleic-acid, 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 5 times. We will report the importance of collapsed state of gels to find these new faculties.

HH2.2
DYNAMICS OF VELOCITIES UNDER HYDRODYNAMICAL CONSTRAINTS: MIGRATION AND TUMBLING. Thierry Beno, Chaoqui Maiba, GREPH, Univ. J. Fourier, Grenoble I, FRANCE.

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

HH2.3
SELECTIVE HYDROGENATION OF OLEIFNS BY DENDRIMER-ENCAPSULATED PALLADIUM NAPHTALOPERIODES. 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 hydroxy-terminated poly(methylacrylate) (PAMAM) dendrimers. These dendrimer-encapsulated catalysts [DECs] were used to hydrogenate allyl alcohol and four substituted derivatives in a 4:1 methanol/water mixture. The results indicate that sterically crowding on the dendrimer periphery, which increases with dendrimer generation, can act as an adjustable-size nanoliter. That is, by controlling the peripheral 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 turnover frequencies (although some interesting exceptions were noted). Although the mechanism of the olefin hydrogenation reactions were the corresponding alkanes, ketones were also obtained when monosubstituted o-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-pentene-3-ol. The effect on catalytic rate as a function of nanoparticle size is also briefly discussed.

HH2.4
SELF-ASSEMBLY OF OLIGOPETIDE-POLY(ETHYLENE GLYCOL) DIHOCK COPOLYMERS, TOWARDS STIMULI-RESPONSIVE DRUG DELIVERY SYSTEMS. Guido W.A. Vandervelde, Heleen-Antonie Blick, Max Planck Institute for Polymer Research, Mainz, GERMANY.

It is well known that the attachment of poly(ethylene glycol) (PEGylation) to a protein stabilizes 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 in 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 't-He-Glu-Ala-Lys-Lys-Ala-Glu' is used, used as a platform for 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, GFC and analytical ultrafiltration experiments and will be described.
POLYPEPTIDE ULTRATHIN FILMS BY VACUUM DEPOSITION: PREPARATION AND CHARACTERIZATION. Timothy M. Fulghum, Roberto Advincula, Jimmy Mya, University of Alabama at Birmingham, Birmingham, AL; Hiroyuki Yamaunari, Hiroyuki Ueki, Kyotaneki 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 range 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 monomer suberate NCA (NCA) benzylserine we have been able to prepare polymeric amino acids for analysis. Benzylserine 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 I peak at 1650 cm⁻¹ and the carbonyl stretching at 1750 cm⁻¹ evidence of the monomer are greatly reduced or disappear in the deposition range of 4×10⁻⁴ mbar mln. 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 45 000 showing a considerably higher degree of polymerization than any other deposition rate. A 450 nm thick film of the films was used to examine the secondary structure. Values of amide I 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 B-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 polymer preparation is being investigated.

Abstract Withdrawn.

METALLIC NANOSTRUCTURES BY PROTEIN TEMPLATING. Silke Behrens, Wilhelm Habicht, Eckhard Dinghas, Dept of Technical Chemistry, Forschungszentrum Karlsruhe, GERMANY, Maria 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 energy levels of 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. Microtubes 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 template. Reducing palladium salts, for example, palladium particles (1-5 nm) are nucleated and immobilized on the tubulin lattice of microtubules.

MESOSCALE COARSE GRANULAR TO ENHANCE HIPOLYMER SIMULATIONS. Dieter Richard 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 automation iteration schemes are introduced to systematically optimize the force field parameters of mesoscopic polymer systems: a simplex procedure and a structure-directed procedure, 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 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 polyacrylic acid are successfully matched with polyelectrolyte light scattering data. For the hydrodynamic radius, the results are in excellent agreement for molar mass up to 300,000 g/mol. Preliminary results for carbonyl (methyl cellulose) will also be considered in this study.

BIOFILM BIOSILIFICATION: PRACTICAL APPLICATIONS TO NANOTECHNOLOGY. Patrick W. Whitlock, Stephen J. Claxton, University of Cincinnati, Deptartment of Materials Science and Engineering, Cincinnati, OH; Rajesh R. Nuk, Lawrence L. Brott, Steve M. Kirkpatrick, Merry O. Stone, Manufacturing and Materials Directorate, Wright-Patterson Air Force Base, Dayton, OH.

In vitro biosilification allows marine diatoms and sponges to produce complex morphologies from siliceous precursors at the nanometer level. The ability to harness this process under laboratory and manufacturing conditions has numerous applications in materials science. Silafins, a set of cationic polypeptides isolated from the diatom Cylindrotheca fusiformis, can generate cylindrical silica nanoparticles when added to a solution of silicic acid in vitro. By incorporating a short synthetic peptide derived from the Silafin 1 (SII) 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 photosilification process. After exposing the cured polymer to a silane precursor, silica nanoparticles are embedded in the peptide-rich regions resulting in a highly ordered two-dimensional array of silica spheres on the polymer backing. The diatom frustule is made of silica nanoparticles that form linear structures, and are primarily responsible for the biogenic formation of silica. The biogenic formation of silica has inspired studies to develop novel inorganic materials that are highly organized and complex fibrous geometries that display remarkable organization at the nanometer sizescale. We are currently investigating the molecular orientation present in these morphologies and developing new methods to control the deposition of silica for nanomaterials.


ENHANCED CYTOCOMPATIBILITY PROPERTIES OF HYDROXYAPATITE DOPED WITH TRIDENTATE IONS. Elizabeth A. Mason, Elliott B. Schmalzried and Thomas A. 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 biocompatibility properties, but is limited in use due to its high solubility within the body and mechanical properties that differ from those of the bone. The present in vitro study investigated the properties of HA doped with a variety of dopants as a way to improve these problematic properties, while maintaining the good biocompatibility 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 hydrogen peroxide. DOPANTS, in the amount of 1% w/w, 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 and 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 had evidenced that HA had 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 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.

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H3.11
SMALL DIAMETER, HIGH SURFACE ENERGY CARBON NANOFIBER FORMULATIONS THAT SELECTIVELY INCREASE OSTEOSTALADHESION. Rachel L. Price, Karen M. Halberstrøm, 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 adherence of osteoblasts (the bone-synthesizing cells); specifically, osteoblast adherence was 35% greater on 155 compared to 200 nm diameter carbon nanofiber composites 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 had no effect on cell adhesion of smooth muscle cell adhesion was 50% less on 125-150 compared to 25-50 mJ/m², which is lower than carbon nanofiber composites after one hour. Collectively, these results provide the first evidence that small diameter and high surface energy carbon nanofibers are novel cytocompatible biomaterials which allow for increased osteoblast adherence and decreased competitive cell adherence for possible improved osseointegration at the implant/bone interface.

H3.12
Abstract Withdrawn.

H3.13

Analogs of dipalmityl phosphatidic acid (PA) and phosphatidylserine-0,5diphosphate [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.

H3.14
MULTIKILOBASE-PAIR AND CHROMOSOMAL DNA SEPARATION ON ENGINEERED INTERFACES. V. Samoilov, Y.-S. Seo, J. Sokolov, M. Rafaihovitch, Department of Materials Science, SUNY-BB, Stony Brook, NY; B. Chu, Department of Chemistry, SUNY-BB, Stony Brook, NY.

Molecular biology applications require long (multi-kilobase pairs) and mega-base pairs (Mb) DNA separation. Traditionally, long DNA fragments are separated by electrophoresis in sieving matrices (electrophoresis on agarose gels or polyacrylamide gels). This process is slow and can 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 LBL technique, to produce patterns at the nanometer length scale, which is not easily accessible by conventional lithography techniques. The micrometer and intermicron distance is controlled by changing concentration of spreading solution and molecular weight of copolymer. This structure was used as a template for introducing specific 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.


H3.15

Optical and non-mechanical properties of an Antarctic sponge Rosella nanovexa were determined using standard optical measurements and a depth-sensing vertical indentation system attached to an atomic force microscope, respectively. The Rosella sponges are 1-2 cm long with a circular cross section of diameter 200 - 600 nm. The sponges are composed of 2-10 nm thick layers of siliceous material that have non-crystallographic characteristics. Optimization of the sponges have interesting optical waveguide properties, e.g., index of refraction, transmission, and angle of acceptance. For example, index of refraction does not change through the thickness, hence, the sponges do not hold graded index refraction. Furthermore, nanomessuresments through the thickness of the sponges also indicated unique mechanical properties (nanohardness and elastic modulus) regardless of layered. Both the chiral modulus and nanohardness values of the Rosella sponges are much higher than that of either fused silica or commercial glass optical fibers. The fracture strength and fracture energy of the sponges, determined by 3-point bend tests, are several times those of sileen rods of similar diameter. These sponge sponges are highly flexible and tough possibly due to their layered structure and hydrated nature of the sponges. These physical characteristics may be due to a possible (protein/silica) molecular composite nature of the sponge sponges as suggested by XPS and TEM/EELS studies. The sponges 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.

H3.16
CALCIUM PHOSPHATE COATING ON TITANIUM PLATES BY ELECTROLEPOSITION. Masahiko Ishikawa, Koju Nasukawa, Kensuke Kuroda, Ichino Ryuchi, Masahiko Okido and Osamu Taki, Nagoya University, CIRSE, Nagoya, JAPAN.

Calcium phosphate films were deposited on titanium electrodes cathodically from CaCl₂·2H₂O and Ca(H₂PO₄)·2H₂O aqueous solutions. In this study, H₂O₂ addition into electrolyte was applied to enhance the electrochemical process at the solution/electrode at a small cathodic potential. The CaP film deposition was analyzed by SEM observation and XRD. Cathodic current of the Ti electrode decreased once and increased in the solution with H₂O₂. It shows a cathodic peak at ca. 25 mV in the case of potentiostatic condition and - 0.756 V (vs. Ag - AgCl, ref. KC1). The calcium phosphate film grows mainly with the decrease in current in the cathodic peak. The characteristics for the electrodeposited film such as crystal morphology depends on cathodic potential, solution pH, deposition temperature and amount of H₂O₂ addition. Dense calcium phosphate film composed of relatively good crystalline was obtained at pH 5.5 and - 0.756 V. Film adhesion on Ti appears to be strong by peeling test. At larger cathodic potential of - 1.156 V, the film coverage on titanium plates is smaller and film adhesion was worsened. Larger cathodic polarization of more than - 1.550V was necessary to reduce water in case without H₂O₂ addition.

H3.17
ARTIFICIAL ZONE OF CALCIIFIED CARTILAGE FROM TISSUE ENGINEERING OF POROUS POLYMER/BIOACTIVE GLASS COMPOSITES. Kui Zhang, Univ of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, Minnesota, Dept of Biomedical Engineering; Theodore R. Osgema, 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 interzone 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 that 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 (>100μm) pores and small (<1μm) interconnected microvoids, instead of the uncalcified cartilage, was used to make porous polymer/bioactive glass composites. Various porous
composites (polysulfone, polyurethane and polylactide) were prepared. The growth of hydroxyapatite crystals (HCA) inside and on the composites proceeded in similar manner and demonstrated the composites bonding ability. In culture, the interaction between chondrocytes and the composites indicates the potential for the composites to facilitate bone 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. Jiacong He, Bing Xu, Department of Chemistry, The Hong Kong University of Science & Technology, Hong Kong, P.R. CHINA; Bingyang Du, Ophelin 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 hydrophilic and hydrophobic monomers (e.g., polystyrene 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 monomer in the mesophase to form the ordered polymer wires or sheets inside hydrogels. The diameter or thickness of the polymer is in the range of few nanometers. We will also describe the X-ray study and the measurements of the optical modulus of these 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.

HH3.20
FORMATION OF BIOAPATITE THROUGH HYDROLYSIS OF CALCIUM PHOSPHATES. Alex Vasquez, Olga Sinitskii, Nosra Pluhik, Valery Putilayev, Yuri Trifyyskoy, Department of Materials Science, Moscow State University, Moscow, RUSSIA.

Bioactive glass-ceramic systems are widely used in modern medicine as implants for restoration, repair and remodeling of dead bone tissue. Many bioactive glasses have been prepared 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 crystallites is believed to be related only to that of bone minerals if one would like to improve biocompatibility of bioactive glasses. Depending upon the technique, powders with various morphology, stoichiometry and level of crystallinity may 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, stabilizers, 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 not always possible to obtain crystals with morphology which are required. The HAp was synthesized through hydrolysis of CaHPO₄ and α-Ca₃(PO₄)₂ precipitation from sol solutions containing Ca²⁺ and PO₄³⁻ ions. The former reaction demonstrated extremely sluggish kinetics and the reaction was limited to the preparation of CaHPO₄. The later led to different phases depending on pH and supersaturation. In some cases the solutions were modified with biocatalysts (gelatin, agar). The modifications drastically influence the size and morphology of crystals. The reactions and products were analyzed with pH, pCa, mechanisms XRD, SEM, TEM, chemical analysis.

HH3.25
ELECTROCHEMICAL SYNTHESIS OF IRON OXIDE TUBES AROUND A BUBBLING TEMPERATURE RANGE. David Stone, Dept of Environmental Sciences, Rad Goldstein, Dept of Physics, University of Arizona, Tucson, AZ.

Iron(III)-based complexes can be brought out of aqueous solution by hydrolysis 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 gas evolving off of an obtained crystal. The bubbles emerge from the tops of the tubes surrounded by a film of basic solution, which rests 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 selforganized, nano-crystalline formations. In the presence of magnetic fields their typical vertical orientation can be altered even to the point of reversing direction.

We are exploring both the physical and chemical properties of this process with the goal of more effectively controlling the growth of the tubes and the chemical stability of the tubes.

HH3.27
MICROSCOPIC CHANNEL FORMATION DURING AN UNSTABLE LANGMUIR-BLODGETT TRANSFER. Kok-Kong Loh, Arvad Saxena, Tarun 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.P. Chi and H. Fuchs, Nature 403, 172 (2000)]. The structure consists of alternating strips exhibiting wettable contrast, creating a microscopic array of micrometer-sized channels with potential microfluidic (nano-fluidic) applications. Using a hydrodynamic description of surface tension deposition at a lateral pressure near the L₁ → L₂ phase transition, this spontaneous emergence of stripe

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

**H3.24** BIODEGRADABLE VESICLES INDUCED BY INTERNAL SALT FLOATING IN LIGHT EMULSION. H. Iri, Y. Hori, K. Yamada, T. Yashima, K. Fujihara, N. Saka, M. Inoue, N. Okada, N. Hori, Department of Biomedical Engineering, Osaka University, Osaka, JAPAN.

**H3.25** DEVELOPMENT OF A CHEMICAL MODEL FOR THE NUCLEATION OF BIOMINERALS USING LESSONS LEARNED FROM THE ANALYSIS OF NATURAL HARD TISSUES. Y.J. Visser, J.V. Prates, W.J. M. Thiessen, J.P. Glaaf, R.J. Prins, J. van der Greef, E. van der Meere, Department of Chemistry, University of Amsterdam, Amsterdam, NETHERLANDS.


**H3.27** EXTRACTED LIQUOR INDUCED HYDROPHILIC TREATMENT OF PET LIGAND TO INHIBIT FIBROBLAST AND COLLAGEN. H. Ono, Y. Hamada, H. Murashita, Department of Plastic Surgery, Gunma University, Gunma, JAPAN.

**H3.28** LOW TEMPERATURE DEPOSITION OF TRANSPARENT ULTRA WATER-REPELLENT THIN FILMS BY MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION. Y. Watanabe, H. Honda, T. Okuda, K. Sasaki, T. Takahashi, T. Hasegawa, K. Tanaka, Department of Materials Engineering, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

**H3.29** INVESTIGATION OF LITHIUM NAPHTHALOCYCLANINE AS A PARTICULATE PROBE FOR BIOLOGICAL EPR OXYMETRY. A. Minawam, Department of Physics, West Virginia University, Morgantown, WV, U.S.A.; Y. Yang, Department of Chemistry, Yonsei University, Seoul, KOREA.

**H3.30** FLOW PATHS IN THE HERALD OF WATER PENETRATION DIFFUSION MEASUREMENTS. H. Tanaka, Department of Chemical Engineering, Brown University, PROVIDENCE, RHODE ISLAND, U.S.A.
Metal naphthalocyanines (MNCs) possess extended \( \pi \)-conjugation systems in their chemical, 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 diltium naphthalocyanine (Li$_2$NC) and monolithium naphthalocyanine (LiNC) based on UV-Visible, X-ray diffraction and EPR techniques. This lithium naphthalocyanine dye aggregate can be simply prepared from Li$_2$NC and LiNC, which demonstrates a suitable candidate for the determination of oxygen in vivo and in vitro electron paramagnetic resonance (EPR) oximetry studies. An oxygen-dependent peak-to-peak EPR line-width ranging from 0.5 to 0.7 G at \( \approx 69 \) mm Hg 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$_2$NC over the other particular probes that are currently being used.

**H3.30**

**COMPLEX MATERIAL USING \( \beta \)-CYCLODEXTRIN AND NICKEL-ZINC FERRITE TO OBTAIN A MAGNETICALLY TARGETABLE DRUG CARRIER.**

Alberto Boccavega,

Rubén D. Sinisterra, Neely D. S. Mohamm, Universidade Federal de Minas Gerais, CTC, 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, limiting toxic effects is often 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 have been derived from the fact that specific ligands can be covalently or ionically bound to the magnetic particles. The strong binding makes the description of these ligands a difficult task and sometimes this approach change the biological activity of the bioactive agents.

The magnetic 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 \( \beta \)-cyclodextrin is externally covalent bound to the Ni-Zn ferrite to obtain a magnetically targetable drug carrier. The physical-chemical characterization was performed through Fourier transformed infrared spectroscopy, X-ray pattern diffractometry.

**H3.31**

**EVALUATION OF THE ADHESION, SUBSTANTIENCY AND ANTIMICROBIAL ACTIVITY OF SUPRAMOLECULAR COMPLEX TETRACYCLINE \( \beta \)-CYCLODEXTRIN OVER DENTIN SURFACE.**

M. Esparza Piedra, Andre Li. Pinto, Carolina P. Franco, Vagner R. Santos, Faculdade de Odontologia Rupén 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 complex tetracycline - \( \beta \)-cyclodextrin (TCP-BCD).

The method used to evaluate the substantivity was by measuring the solution samples by ultraviolet visible spectrophotometry. The morphological effects of tetracycline were determined by scanning electron microscopy. Antimicrobial activity was determined by Minimum Inhibitory Concentration (MIC) on Gram positive strains. The results measured were: 100% in the solution samples by ultraviolet visible spectrophotometry. The morphological effects of tetracycline were determined by scanning electron microscopy.

Electrospinning produces fibers having diameters in the range of hundreds of nanometers. In the last twenty 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 turn and elevation changes. Fine control can be achieved by controlling fiber orientation resulting from electrospinning. The electrosprun wing simulation that mimics the performance of a bird or bat wing. Various electroactive polymer blends have been electrospun. The properties of the polymer blends, including tensile strength and Young’s modulus, were measured for the blends.
electro spun 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 entire wing.

**H3.35**

**HYDROGEN-BASED SELF-ASSEMBLED “ELECTRICALLY WIRED” ENZYME MULTILAYERS IN REAGENTLESS BIOSensors**

Ernesto J. Calvo, Claudia Danielewicz, Erica Formani, Alejandro Velev, and M. INGUAMA C. Facund, 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 Diazin polyphenylmione (PAM-0s) have been assembled. Spatially mapped enzyme and redox polyelectrolyte assemblies offer several advantages over the use of enzyme electrodes for electrochemical and optical analysis measurements to study the build-up and behavior of these self-assembled multilayers. Upon change of redox state in the Os(IV/I) polymer by electrochemical perturbation, the thickness and viscoelastic properties have been found to be sensitive to the redox condition, and in situ monitored by quartz crystal microbalance. For films which resulted actually thin, the mass change due to the exchange of ions and solvent with the external electrode was correlated to the amount of electrical charge and the nature of the overall process unravelled.

**H3.36**

**FORMATION OF SUPRAMOLECULAR ASSEMBLIES BY MODULATING SELF-ASSEMBLING PROPERTIES OF DIACETYLENIC PHOSPHOLINeS**

Alex Singh, Mark S. Spector, Joel M. Schur, Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington, DC.

Considerable efforts have been devoted to understand and control the formation of supramolecular morphologies in bilayer 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 charged, amphiphilic phospholipid, 1,2 bis (triacetoxy-1,1,1-trimethyl)-3,6-diacylphosphocholine. We have been able to control the morphology of preassembled structures by making small chemical changes in the vicinity of diacetylenic functionality by chemical or physical means. One such modulation has led to the formation of nanotubules (nanometer diameter) and nanohelixes. 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 transformed into microstructures. We have also observed field-induced polymerization in nanotubes as opposed to their micro counterpart suggesting a different molecular arrangement in the supramolecular architecture. Polymerization renders diacetylenic-based morphologies physically stable and help in performing chemistry as their surface to make them technically attractive. We will discuss synthesis and characterization of nanotubules and helical supramolecular assemblies.

**H3.37**

**FORMATION OF ORIENTED CALCIUM PHOSPHATE STRUCTURES ONTO SELF-ASSEMBLED TEMPLATES BY A SOLUTION-PURIFIED NUCLEUS MECHANISM**

Barbara J. Tanasech, Shari Li, Pacific Northwest National Laboratory, Richfield, WA; David L. Alhara, Pennsylvania State University, University Park, PA.

The nucleation and growth of calcium phosphate is of great importance to the formation of mineralized hard tissue structures such as bone and teeth and for unwarranted, ectopic calcium phosphate deposition on or in the body. Important to 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 on model nucleation template composed of penicillin G immobilized on gold that were developed and tailored to have various surface functionalities, various surface site densities composed of mixtures of two thiol, and various degrees of conformational disorder compared to mixtures of various chains long. This was studied from physiochemical and solutions as well as simpler solutions. Kinetic studies using an in-situ microscope, absorbance studies using X-ray photoelectron spectroscopy, and solution studies reveal that the nucleation and growth of calcium phosphate on SAMs involved the adsorption of solution-formed calcium particles. 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 bio mineralization, on orientation, and on the synthesis of complex calcium phosphate structures will be discussed.

**H3.38**

**IN SITU OBSERVATION OF NUCLEATION AT INTERFACES: SYNCHROTRON X-RAY STUDIES OF BIOLOGICAL MINERALIZATION STUDIES**

Eliane DiMarino, Brookhaven National Laboratory, Upton, NY; Matthew M. Pawel, Lockheed Martin; Jane Beanbarger, ETH Zurich; 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 titania oxide substrates, modified by bone implant materials. The second study presented is of mineralization in 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 how an organic matrix can or should be considered a “template” for mineral nucleation.

**H3.39**

**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 is part of 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 membranes-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 zinc. Zinc is smaller than calcium and might be thought to replace calcium in calcification. The solid products were characterised by X-ray diffraction, transmission and scanning electron microscopy, X-ray energy dispersive analysis, infrared spectroscopy and thermal gravimetric analysis. Zinc ions have been found to have a striking influence on the morphology and crystallinity of precipitates of calcium pyrophosphate. The undoped particles are observed in the form of small crystals as discrete orthorhombic plates. The doped material is characterised by agglomerates of morphic spherical particles. Our observations suggest that the control of the ion, rather than the complexity of the biological system, can regulate the morphology of these compounds.

**H3.40**

**DEVELOPMENT OF VINYL ETHER LIPIDS FOR PHOTOTRIGGERABLE PHIBRINOGEN HYDROGELS**

Jinghua Shen, David H. Thong, Po-Chi Sun, Chyi-Yi Zhang, Purdue University, Dept of Chemistry, West Lafayette, IN.

We have developed an extension of the “cradle” triggering method for producing rapidly gelating fibrinogen-based protein hydrogels using photosensitive calcium-loaded liposomes that is similar in concept to a system reported by Westhusus and Messersmith. The liposomes were prepared by interdigitating-fusion liposomes (1FL), comprised of 38 mol% dipalmitoylphosphatidylcholine (DPPC), 17 mol% dodecylphosphatidylcholine (DSPC), and 5 mol% bacteriochlorophyll (Bohl). The liposomes were encapsulated by 10 mg/mL NaClO2. Continuous irradiation of DNA,
400mW/cm² of these liposomes under aerobic conditions lead to the photocatalytically induced leakage of greater than 90% of entrapped Ca²⁺ within multilamellar vesicles (MLVs) of 1000 Å and a Ca²⁺-dependent transglutaminase enzyme remained fluid in the dark, but gelled rapidly when irradiated in the presence of air at 800nm and 37°C. SDS-PAGE analysis of the reaction mixture showed that gelation was due to transglutaminase-mediated crosslinking of the fibroin α- and γ-chains. Cryo-SEM analysis of the resulting hydrogel revealed a sponge-like network structure with pore diameters ranging between 4.8 µm and pore walls of 0.1-µm thickness. Photocatalytically liposomized indocarbocyanine (IR700)-labeled phasophyllinolipid precursors can also be used to activate this system. Potential applications of this photoactivatable hydrogel system in drug delivery will be discussed.

References:
1. The authors would like to acknowledge the support of NIH Grants GM55266 and DE 13080.

**HH3.41**

**DEGRADATION STUDY OF AMPHIPHILIC STAR-LIKE MACROMOLECULES**

Jing Wang, Kathryn Ulrich, 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 macromolecular nanocarriers. Linked by ester and amide bonds, which are susceptible to hydrolysis, ASMs are thermodynamically more stable than conventional micelles. They are also biocompatible and biodegradable, meeting the requirements of drug delivery systems. In this study, the degradation of ASMs was investigated at 37°C in a sodium phosphate buffer solution at pH 7.4 in the presence of cholestearin (EC 2.4.2.27) 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 products 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 under polymer degradation begins, which means the ASMs can be a good candidate for drug release material.

**HH3.42**

**FLUORESCENT SILICA NANOPARTICLES FOR SINGLE PARTICLE TRACKING EXPERIMENTS ON RAT MAST CELLS**


Single particle tracking (SPT) has been developed in recent years to evaluate lateral diffusion of individual components on cell surfaces. This method has allowed for 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 nonspecific binding. This study examines synthesis, synthesis, and characteristics 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 Stoeger et al., with modifications necessary to conjugate organo-Si molecules of interest 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 conjugation of silica nanoparticles with different sizes and the successful development of assay methods.

**HH3.43**

STRUCTURAL AND BIOPHYSICAL STUDIES OF HALACESTANT LUNG SURFACTANTS: Heidi Warriner, Jungi Dong, Joe Zarembinski, Chemical Engineering Dept, UCSD; 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 inspiration. Neonatal Respiratory Distress Syndrome (NRDS), caused by the absence of lung surfactant in premature infants, can be treated via transbronchial installation of replacement surfactant. Halacestant, a lung surfactant monolayer that 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 blood proteins can inactivate a surfactant monolayer by increasing interfacial pressure above the critical regulating 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 surfacants by the new lipids.

**HH3.44**

**IMAGING OF SUBSURFACE DEFECTS IN BIVALVE MOLLUSK SHELLS BY PHOTOTHERMAL TECHNIQUES**

Octavio Gómez-Martínez, Miguel Zambrano-Arjona, J.J. Alvarez-Gil, Cinvestav Unidad Mérida, Dept. of Applied Physics, Mérida, Yucatán, MEXICO.

The potential of photothermal radiometry for the subsurface defects imaging in bivalve mollusk shells of Crassostrea virginica and Ischindrum 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 large 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 MUSTELID ISCHINDRUM RECURREN (RAPHINESQUE, 1820) (MOLLUSCA BIVALVA)**

Daniel Aguilar, Octavio Gómez-Martínez, Juan J. Alvarez-Gil, Patricia Quintana, Cinvestav Unidad Mérida, Dept. Applied Physics, Mérida, MEXICO; Damián Arzenda, Geogyra Gómez-Castro, Cinvestav Unidad Mérida, Dept. of Sea Resources, Mérida, MEXICO.

X-ray diffraction analysis of the texturization development of the shell of the mussel Ischindrum recurvum (Raphinesque, 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 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**

**PHOTOCHEMICAL MINERALIZATION OF TYPE I1 COLLAGEN**

Matthew Okato, Dongso Kim, Elliot Douglas, and Laurie Gower, Department of Materials Science and Engineering, Gainesville, FL.

In order to produce novel biomaterials, such as bone graft substitutes, for critical-sized caveous 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 bioabsorbable 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 (0.5-2.0 μm in diameter), we have deposited calcium carbonate tablets and films on the surface of the fibers. The tablets, which are approximately 20 to 30 μm in diameter, and half a micron thick, appear to be aligned in rows perpendicular to the axis of the collagen fibers. In subsequent studies, the reduction of the collagen fiber size to 20-100 μm produced calcium carbonate films that covered the fiber length. Further development of such films by the traditional rhombohedral calcite morphology. Continuing research is also being performed on various other type-I collagen, including collagen and tendon from domestic turkeys (which mineralize naturally). In the latter case, the collagen is to form a microstructure in biological systems (i.e., aligned and oriented nanocrystalline).

**HH3.47** MECHANISM OF PHOTOCHEMICAL CALCINATION OF SURFACTANT-TEMPLATED THIN FILM SILICA MESOPHASES. Andrew M. Dzubiella, Meni Aviram, John D. Ruiz, Laurel E. Ecke, Andrew B. Stare, Bioscience Division, Los Alamos National Laboratory, Los Alamos, NM, Atul Parikh, Department of Applied Science, University of California, Davis, CA.

We have explored 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 reproducibly 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 25 mm/μm from a sub cm solution mixture containing mesogenic surfactant and, TEOS, a silica precursor. We observe that surfactant removal, silica reconstruction, and film shrinkage occur gradually and consecutively. 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 control photocalcination further suggests that simultaneous presence of UV and ozone is optimally needed for efficient photochemical calcination. 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 POLYSTERENE SPHERES IN SPRAY-DRIED PARTICLES INCREASES THEIR POROSITY. Nicolas Trois, Dave Weitz, DEAS, Harvard University, Cambridge MA, David Edwards, Advanced Information 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 the same hydrodynamic radius, as measured by an Aerokim, whereas the geometric radius, as measured by light scattering, is around 5 nm. The geometric size of the spray-dried particles increases as PS spheres are added to the sprayed solution, which means that up to 50% of PS spheres, on average, are too large to be solubilized in solution. On the other hand, the hydrodynamic 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-Universidad Merida, Dept Applied Physics, Merida, MEXICO; Martin Varela-Linora, Laura Díaz-Flores, Centro de Biotecnología, Merida, Yucatan, Merida, MEXICO.

Fourier Transform infrared spectroscopy has been employed to study the shell of two kind of mollusks, american oyster (Crassostrea Virginica) and mussel (Ischadium Recurrum). 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 amorphous 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. Vinal Patel, Matthew Obata, Laurie Gower, University of Florida, Dept of Materials Science and Engineering, Gainesville, FL; Elhine Dibiasi, 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 Laboratory 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 super saturated 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 amorphous to crystalline transformation.

**HH3.51** PATTERNED CALCITE FILMS FROM A POLYMERICALLY PRECIPITATED INORGANIC-POLYMER PHASE USING MICRO-CONTACT PRINTING. Yi-Young Kim, Laurie Gower, Department of Materials Science & Engineering, University of Florida, Gainesville, FL.

An important feature of biological crystallization is perfectly controlled over the microenvironment of crystal growth. In fact, certain organisms have evolved the ability to produce organized crystal scaffolds sequentially deposited into two-dimensional 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 biomimetic crystallization. Precise localization of particles, nucleation density, size and morphology are important parameters that affect the performance of inorganic materials. To-date, we can control over all of these properties by sequentially depositing an inorganic polymer on to a calcite film and then the pattern calcite films grow under constrained conditions via transformation of the PILP phase. This work is supported by NSF grant BES-9802795.

**SESSION HH4: BIOPOLYMERS**

**8:30 AM **HH4.1 MECHANICAL REGULATION OF THE FUNCTIONAL STATES OF PROTHRINS. Viola Vogel, David Craig, Wendy Thomas, Andre Kranner, Grethe Bille-Mortensen, Arne Baegaard, 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 fibronectin 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 FnII-1 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 fibrinogen in cell culture.


Structural and compositional control of materials at the molecular scale is a key feature 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, bone tissues (bacterial spores, 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 biomimetic material systems for practical technological applications is to engineer proteins for use as molecular ionic erectors 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 (GEPs) have potential significant implications in tailoring surfaces, assembly of ordered and complex nanomaterials of metals, functional ceramics, polyelectrolytes, and combinatorial organic and inorganic architectures. At low multivalent ionic concentrations, a homogeneous solution of uncondensed filaments is observed. At high multivalent concentrations, the filaments condense into bundle-like structures, in the form of rods or tubes, which can be used to form an intermediate material. In this sense, two charged macromolecules can condense into hierarchical organized tubules with no direct analog in simple membrane systems. Using high resolution small angle X-ray scattering, confocal microscopy and electron microscopes, we will present a systematic structural investigation of these condensed biopolymer phases, and the resultant implications for new materials.

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

Hydrogels were fabricated from triblock artificial proteins consisting of two hydrophobic leucine zipper end-blocks and a hydrophilic random coil middle block. Self-assembly of the kucine 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 hydrogel allows engineering of new domains for cell binding and enzymatic recognition, relevant to potential biomedical applications. To achieve rational designs of tunable 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 desired for use as an ideal neural tissue engineering matrix. 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 elastic 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 middle block. We are able to show that increasing the contour length or charge density of the middleblock, or raising pH to improve solvent quality for the middleblock, are effective ways to increase moduli at low concentrations. We also studied the dynamics of these transient networks. Bioregulated measurements using the nanoscopic relaxation time and exchange experiments by fluorescence quenching and relaxation techniques yielded the dissociation rate of the leucine zipper domain. By probing these results, we observed a correlation between nanoscopic processes and molecular dynamics on a macroscopic 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. Lance Sternak, Akh Singh, Center for Molecular Sciences & Engineering, Navy Research Laboratory, Washington, DC.

Polymerized vesicles, which are submicron, water-dispersible capsules composed of amphiphilic surfactants covaiently stabilized into bilayers (~ 5 nm) structure, provide for a useful scaffold to immobilize functionally relevant hydrophilic and hydrophobic materials. Our focus is to stabilize and interface these structures composed of biomimetic polymers in an electrochemical manner, a desired level of vesicle electrolytivity. 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 organic 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 BIO-POLYMERS, MEMBRANES, AND COUNTERIONS. Gerd CL. 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 MJ3 viruses. For example, F-actin can form a smart gel with tunable architecture. At low multivalent ionic concentrations, a homogeneous solution of uncondensed filaments is observed. At high multivalent concentrations, the filaments condense into bundle-like structures, in the form of rods or tubes, which can be used to form an intermediate material. In this sense, two charged macromolecules can condense into hierarchical organized tubules with no direct analog in simple membrane systems. Using high resolution small angle X-ray scattering, confocal microscopy and electron microscopes, 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, Elin Benirsch and Samuel I. Stupp, Northwestern University, Dept. of Materials Science & Engineering and Dept. of Chemistry, Evanston, IL.

A series of peptides-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 solution 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 native uncondensed peptide amphiphile and the ability to form at a 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. 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 microstructure 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 STRUCTURE AND FUNCTION OF SYNTHETIC POLYPEPTIDE MATERIALS. Hans-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 efficiently 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 developed for the self-assembly in this manner, materials with unprecedented control of structure and function of synthetic polypeptide materials. By virtue of their ability to form directed hydrogen bonds, peptides could drive the self-assembly of synthetic polypeptide into well-defined superstructures. In addition, the sensitivity of the secondary structure of certain peptides towards
temperatures, pH or ion-strength, could allow access to novel stimulioresponsive 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 co-condensation of polymer chemistry and bioorganic (solid phase) synthesis. The first example will discuss the properties of tyrosine-rich peptide copolymers. In the solid state, these molecules form thermotropic liquid crystalline phases. Unlike 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 peptide segment organization. The potential of these materials for applications in biomedicinal technologies will be discussed.

11:30 AM HH4.8
MONOCLONAL ANTIBODY RECOGNITION OF A HISTIDINE-RICH PEPTIDE ENCAPSULATED NANOCLUSTER. Joseph M. Stock, 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 digestion of hemep, Cu and Zn. For example, the fangs of marine polychaetes contain histidine-rich proteins that mineralize with Zn in concentrations of as high as 35% 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 metal sulfide, metal oxide and zero-valent metal clusters. The clusters have been characterized by UV-visible and fluorescence spectroscopy and transmission electron microscopy. Additionally, the purified nanoclusters have been shown to be immuno-reactive with a monoclonal antibody for the specific HRP II epitope.

11:45 AM HH4.9
SELF-ASSEMBLY OF L-SHEET PEPTIDE INTO NANO-HELICAL RIBBON INTERMEDIATE AND NANO-HELICES. Dawid Marini,*2 Shuangying Zhou,2 Wenzek Hwang,2 Douglas A. Laffrenier1 and Roger D. Kamm1,3,5 Dept of Mechanical Eng; 2Ctr for Biomedical Eng; Div of Biengerg and Environmental Health, Massachusetts Institute of Technology, Cambridge, MA.

Short peptides, designed with a repeating sequence of hydrophilic-hydrophobic amino acids, have been shown to self-assemble into stable, three-dimensional networks of fibers characterized by a 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 FK85. The self-organization of FK85, from a monomolecular to nanofibers and nanofiber networks, was followed over time using atomic force microscopy. In the early stages of initiation (minutes) this molecule forms regular nanofibers exhibiting a "helical ribon" 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 complex of molecular self-assembly. These findings have significant implications for applications in the molecular design of nanomaterials. Furthermore, these peptide nanofibers share the characteristic features of b-amylloid fibers, thus providing a new model system to study amyloid fibers formation and other protein conformational diseases.


1:30 PM *HH5.1/AA5.1
MULTIPHASE ASSEMBLY AND PROCESSING OF COMPLEX COMPOSITE MATERIALS. Michael Wong, Jennifer Chu, Lorcan Eades, Scott Curtin, Eric Chau, 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 copolymers and protein molecules provide a particularly useful synthetic approach to the design of materials with unique properties, including the 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 chain parameters that can be obtained with block copolymer or polypeptide - non-ionic polymer linkages. Block copolypeptides and their congeners also provide a convenient route for the incorporation of chirality or cholesteric stereocomplexity, and the temperature use of their secondary structure (helical or ribbons) in composite assembly. The processing of block copolypeptides or polypeptide composite based materials can be carried out with nanoscale extrusion using mesosporous arrays as templates. These composites can be used as a large variety of multi-component domain configurations. An example is the single step assembly using block copolypeptide polymers with specific binding affinities to metals, metal chelates, and metal oxides to produce defined nanoscale materials. The exploitation of these composites promise a new generation of well-defined microstructures such that nanocomposites of one composition are spatially oriented in non-aggregated and organized arrays that are completely interior or exterior of 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
ELEVATING THE MOLECULAR CONTROL OF SEMICONDUCTORS AND MAGNETIC NANO-STRUCTURES. Angela M. Becker, Christine 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 and mechanisms underlying biological molecular recognition in materials and developing new strategies to pattern useful 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 wafer her and semiconductor and magnetic nanoparticles. This approach utilizes the inherent self-organized, highly selective properties of biologically designed molecules. We are currently investigating protein self-assembly and interaction with III-V and II-VI semiconductor materials and magnetic nanoparticles. We have selected peptides that can nucleate and control crystal 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

Using surfactant-mediated self-assembly, a large variety of organic functions can be incorporated in silica-based nanoparticles in order to create organo materials that can find applications in fields ranging from adhesion, 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(OR)3)] and [(OE1-Si(OR)2)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 has been performed by means of XRD with synchrotron radiation, one- and two-dimensional multidimensional NMR and adsorption-desorption experiments. Depending on the nature of the precursor and on the experimental conditions (pH, nature of the solvent), 2D-hexagonal (p6m) as well cubic (Pn3m) phases have been obtained and we have tried to understand the role that the R group could play in the self-assembly. Then the synthesis was extended to dip-coated thin films using evaporation induced self-assembly, and once again, we investigated the morphology and structure of the film by XRD and the interrelation of the film structure, determined by 3D XRD techniques, and chemical parameters.
An amphiphilic diblock copolymer, poly(isoprene-b-ethylene oxide) (PI-b-PEO), was used as a structure-directing agent for an inorganic alumina (Al₂O₃) powder in order to generate a variety of highly ordered inorganic-organic nanocomposites. The resulting order and morphology in 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 organic (IO) 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 calculated to form mesoscopic materials with potential applications in the fields of catalysis, separation technology and microelectronics. The mesoscopic microstructures resemble periodic minimal surfaces; discriminating between these similar yet distinct morphologies can be a subtle task. This task concerns us on the phase diagram region of the ordered continuous structures using a combination of small-angle x-ray scattering (SAXS), transmission electron microscopy (TEM), and gas adsorption measurements.


3:15 PM *HH5.5/A55.8

BIO-INSPIRED NANOCOMPOSITES: FROM SYNTHESIS TOWARDS POTENTIAL APPLICATIONS. Tewodros Asefa, Neil Cooper, Hikrad Gredlew, Materials Chemistry Research Group, Department of Chemistry, University of Toronto, Toronto, Ontario, CANADA. Michael 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 mesostructured organosilicas (PMO) materials are an entirely new class of silica material with mesostructures inorganic networks, high surface areas and pore volumes, and well ordered and uniform size pores and channels. We have recently extended the synthesis to include macroporous 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/A55.8

PREDICTING THE MESOPHASES OF COPOLYMER/ NANOPIRATE COMPOSITES. Russell Thompson, Anna Baker, University of Pittsburgh, Chemical Engineering Department, Pittsburgh, PA; Valerie Ginzburg, The Dow Chemical Company, Midland, MI; Mark Masen, University of Reading, Polymer Science Center, Reading, United Kingdom.

The interactions between mesophase-forming copolymers and nanoscopic particles can lead to highly ordered hybrid materials. The morphology of such composites depends on the characteristics of the copolymer and the features of the nanoscale. To date 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/A55.7

SELF-ASSEMBLY MECHANISMS INVOLVED IN THE FORMATION OF SO₄, TiO₂, Al₂O₃, ZrO₂ AND V₂O₅- Mesostructured Hybrid Films as Revealed by In-Situ SAXS Analysis. David Grosso, Galk J. de A. Scler-Illia, Eduardo Crepaldi, Ludovine Pielot, Florence Bahonneaux, Clément Sanchez, LCMGUMP-CNRS, Paris, FRANCE; Pierre-Antoine Albalou, LIPS, Université Paris-Sud, FRANCE; H. Amenitsch, Institute of Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Graz, AUSTRIA.

The formation of mesostructured 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 multiphase systems. However, this method has proven to be relatively robust and reproducible as long as the composition of surfactant can be controlled. The preparation of mesostructured thin films by liquid deposition techniques is further complicated by other parameters which are the liquid phase evaporation, the presence of film/solvent interface and the capillary and swelling forces existing at these interfaces. In this work, we studied the self-assembly mechanisms taking place during dip-coating of SO₄, TiO₂, Al₂O₃, ZrO₂ and V₂O₅ templated films exhibiting the p6mm hexagonal structure. Initial solutions were prepared from methanol in which was dissolved the inorganic precursors and the Brje 98 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 mesoorganization 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/solvent and film/solid interface play key role in the orientation of the organized domains.

4:15 PM HH5.8/A55.8

IN-SITU X-RAY SCATTERING STUDIES DURING EVAPORATION INDUCED SELF-ASSEMBLY OF SILICA SURFACTANT NANOSTRUCTURES/MESOPHASES. Dhruv A. Doshi, Nanguo Liu, Hongji Chen, Department of Chemical and Nuclear Engineering/Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM; Valerie Goette, University of Paris, Paris, FRANCE; Darren Duphily, Scott Reed, Sandia National Laboratories, Albuquerque, NM; Andrew MacPhee, Suresh Narayanan, Jim Wang, Advanced Photon Source, Argonne National Laboratories, IL; Benjamin Ocko, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY; Abin Hurd, Los Alamos National Laboratory, Los Alamos, NM; Alan Givens, University of Maine, ME; Argonne 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 ubiquitous in nature. From the cell membrane to detergent soap bubbles, their uses are endless. Kresse 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 nanomaterials. 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 and a surfactant the 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/A55.9

NONAFFILIATION OF INORGANIC MATERIALS USING CATIONIC LIPID-BIOPOLYMER SELF-ASSEMBLED SYSTEMS. Hongjun Liang, Thomas E. Angellis, James He, Paul V. Braun, Gerard C. Le Wieg, University of Illinois at Urbana-Champaign, Department of Materials Science and Engineering, Urbana, IL.

It has been shown that cationic lipid-DNA complexes can selectively fuse into a nanoscopic lamellar structure, in which DNA ordered DNA arrays are intercalated between planar lipid membrane sheets. The DNA springs can be tuned from 2.5nm to 6.8nm, 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 GIS and related compounds, by variation of parameters such as the membrane charge density, the ratio of DNA-lipid 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 composites. Preliminary results on the morphologies of the templated phases as a function of these parameters will be presented.

4:45 PM HH5.10/A5.10
PHOTOCHEMICAL PATTERN TRANSFER, ENHANCEMENT, AND RECOGNITION IN THIN FILM SILICA MESOPHASES. A.M. Decurtins, Lauret,Ecke, Robert A. Provenal, 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 (18-254 nm) generated ozone environment, provides an efficient method for the removal of surfactant templates for a routine production of well-ordered, mesoporous silicon thin films at low temperatures. The treatment concurrently strengthens the silicate phase by fostering the condensation of surface SiOH groups leading to the formation of thin films with well-defined mesoscopic morphologies. Here, we show that this photochemical "calcination" process lends itself for convenient removal of surfactants in internal or externally defined regions at micrometer length scale. This method is ideal for defect-free thin film formation. 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) lends to significant pattern enhancement and pattern recognition. Potential uses of patterned mesoporous silicon thin films will also be discussed.

SESSION HH16: 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 NANOFACTURED 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. To realize such devices, one needs to take 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, evolve and reproduce. A critical part of our efforts to incorporate biological energy transduction processes and cell signaling pathways into engineered nano-fabricated devices is the preservation of the necessary components of the cells. In particular, we will illustrate our strategy for fueling, controlling and integrating a recombilant, thermogenic FI-ATPase molecular motor with a NEHS to create an engineered hybrid device. Included in the presentation will be the initial results of our efforts to develop and demonstrate an integrated FI-ATPase powered NEHS 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 F1-ATP synthase and bacteriorhodopsin. Subsequently, the ATP is used to provide energy to power the recombilant, thermogenic FI-ATPase biocatalytic motor (ca. ~12 nm) that is coupled to a NEHS device. Our current analysis indicates that a light collection area as small as 500 nm² will provide enough energy to power each FI-ATPase biocatalytic motor. Since the number of ATPase biocatalytic motors can generate a torque consistent with the force required to move engineered nanomachines, we will also present our technique for integrating nanomechanical structures to biocatalytic motors with a precision ~ 10 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 NEHS establishes a new mechanism for fueling the next generation of nanomechanical devices. Light is used to produce ATP, which can be used by the NEHS to drive the FI-ATPase biocatalytic motor or to produce work with ADP and Pᵢ as 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, Yuxia Li, Seok-Ho Kang, Cornell University; Dept. of MSE & RIT, Ithaca, NY; Edward J. Kramer, Alex Hehremer, Eran Sivanath, 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 polymer systems. As an example of this 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. Nonetheless, the best strategies 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-co-1,2,3,4-tetrapropylene). 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 some of the results of these studies 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 UTA beamline at Brookhaven National Laboratories are appreciated.

9:30 AM HH6.3
BIOFILM WATER-REPELLENT SURFACES PREPARED BY USING MICROSTRUCTURES OF PHASE-SEPARATED POLYMER MIXTURES. Osamu Takei, Jun Inui, Yasushi Inoue, Hiroyuki Sagimura, 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 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 organosilicone compounds as raw materials. These films 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 on the substrate. In this work, we have developed a new method to prepare water-repellent surfaces based on the nanorough structure of a spin-coated layer of phase-separated polymer mixtures covered with a hydrophobic thin layer. We fabricated the polymer layer with the nanorough structure on glass substrates by dissolving one of the phases in the spin-coated polymer mixtures of poly(methylmethacrylate) (PMMA) and polystyrene (PS). The hydrophobic layer was deposited by PECVD using tetramethylsilane (TMS) as a reactant. Surface morphology, water wettingability and chemical bonding states of the films were characterized by using AFM, a static contact angle meter and FTIR. An environmental scanning electron microscope (ESFM) was used to observe the appearance of micro water drops on the surfaces. AFM observations show that the nanorough 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. ESFM observations show that the contact angle is locally much higher than the macroscopic value. This work is supported by 3JSPS-RFTF98R13101.

9:45 AM HH6.4
Rapid, Sensitive, Selective Biosensor Using A SQUID MICROSCOPE. Helene Grossman, Yarn Chemla, Yaron Poon, Richard Bruehl, Carolyn Bertozzi, Raymond Stewart, John Clarke, and Muki Adler, Departments of Physics, Chemistry and Material and Chemical Biology, University of California at Berkeley, CA; Department 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 ultrasmall
"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 magnetic 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 (milliseconds)
by Brownian motion and are not detected. On the other hand, the
signal from immobilized particles bound to targets slowly relax by the
Néel 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
method has been developed to improve the sensitivity by up to two orders of magnitude, thereby
allowing detection of as few as 50-100 particles. The number of
magnetic labels is determined by the number of targets present, and the number of
many magnetic particles bind to each target.

Supported by U.S. DOE Contract DE-AC03-76SF00008

10:45 AM *HH6.6
NEW RESULTS ON ACTIVE MEMBRANES. G. Giraud1, J. Derryn1, F. Juilhier1, S. Ramasamy1, A. Roux2, G. Cappello1, P. Bassereau1, B. God3, J. Prens1, Curie Institute, Section de recherche, Paris, FRANCE. 1Curie Institute, Section de recherche, Paris, FRANCE. 2Indian Institute of Science, Phys Dpt, Bengaluru, INDIA.

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

10:45 AM *HH6.6
REGULATING CELL SURFACE INTERACTIONS WITH AMPHIPHILIC COPOLYMERS. Anne M. Hayes, Darrell J. Irvine, Dept of Materials Science and Engineering, MIT, Cambridge, MA. Linda G. Grunwald, Dept of Chemistry and Biological Engineering and Environmental Health, MIT, Cambridge, MA.

The objective of our research is to develop facile methods for
fabricating monolayers that are maintained out of equilibrium by the action of pumps or of kinases moving on
microtubules.

11:45 AM HH6.9
DNA-DIRECTED ASSEMBLY OF METAL PARTICLES. Christine Kesting, Brian Reiss, Shelia Newcomer, 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 temperatures-dependence of this process. DNA has been attached to the surface of gold particles as well as metal nanowires several microns in length, and the ability of this particles-bound DNA to selectively and reversibly bind complementary DNA 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 on 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 biocatalysis 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 the deterministic construction of nanostructured materials. We are particularly interested in the
potential of DNA hybridization in directing 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 decorate 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.

11:45 AM HH6.7
ENGINEERING DNA-BASED SURFACES FOR DIRECTING ASSEMBLY. Paul Lashaw, Ivan Lee, Manish Buij, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

We have developed methods for generating surfaces expressing
covisually gated, 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 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 allylamine monomers that also expose both reactive hydroxyl groups and inert methyl groups. Control over
surface composition and sequence afforded 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.