

15-01

Non Classical Crystallization

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In recent years, increasing evidence is reported that many crystallization events do not obey the laws of classical crystallization i.e. an ion or molecule attachment to a critical crystal nucleus. Starting from the consideration of biominerals with their often complex forms and several levels of hierarchy, a view of particle mediated crystallization events is developed, often starting with amorphous precursor nanoparticles. These precursor particles undergo mesoscopic transformation to nanocrystals and assembly processes to superstructures with complex shape. Some of such intermediates called mesocrystals are shown, which could explain the inclusion of macromolecules in single crystalline biominerals. Subsequent crystallographic fusion of mesocrystals can lead to single crystals with preserved shape. Direct nanoparticle fusion according to the mechanism of oriented attachment can directly lead to single crystals, which will be demonstrated. Also, Polymer Induced Liquid Precursors (PILP's) will be shown as precursor species in non-classical crystallization events leading to complex morphologies for the case of amino acid crystals.

15-02

Principles of Biominerals Architecture: Nucleation Mediated Self-Assembly Of Biomineral Crystals

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Bones and teeth are biocomposites which are self assembled in a certain manner that require controlled mineral deposition during their self-assembly to form tissues with unique mechanical properties. Various biomolecules play a pivotal role during the formation biomineral nano crystallite assembly. However, the mechanisms of biomolecule-mediated mineral initiation are far from understood. In this contribution, I will present that the formation of the well-aligned hydroxyapatite nano crystallite assembly is controlled by the so-called self (homo)-epitaxial nucleation mediated assembly (SENMA) mechanism, which unfortunately will be demolished at high supersaturations due to the unflavored kinetics (supersaturation driven structural mismatch). It is identified for the first time that biomolecules, e.g. chondroitin sulfate, facilitate the formation of a well-aligned HAP assembly by suppressing the supersaturation driven structural mismatch rather than by “cementing” HAP crystallites.

15-03

Noncovalent Functionalization of Carbon Nanotubes Using Designed Peptides

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To fully realize the potential utility of carbon nanotubes, strategies for the effective solubilization, separation and organization of these materials must be devised. In this presentation the use of designed amphiphilic peptides to achieve these goals will be described, with a focus placed on the peptide design, as well as the characterization of the resulting peptide/nanotube composites. Results from circular dichroism, Raman, UV/Vis/NIR, SEM and TEM studies will be discussed which demonstrate that designed amphiphilic peptides are effective at solubilizing carbon nanotubes in aqueous solution, debundling the nanotubes yielding long individual nanotubes, and organizing them into different macromolecular architectures depending on solution conditions. The ability to control nanotube organization by utilizing the self-assembly properties of the peptides provides a facile and versatile method for the manipulation of carbon nanotubes for future applications.

15-04

Manufacturing with Micro-organisms: Merging Biological Self-Assembly with Synthetic Chemistry to Yield Functional 3-D Nanoparticle Structures

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Appreciable global effort is underway to develop new routes to three-dimensional (3-D) nanostructured devices. To enable widespread commercialization, such processes must be capable of: i) precise 3-D fabrication on a fine scale and ii) mass production on a large scale. These often-conflicting requirements can be addressed with a revolutionary new paradigm that merges biological self-assembly with synthetic chemistry: **Bioclastic and Shape-preserving Inorganic Conversion (BaSIC)**. Nature provides spectacular examples of micro-organisms (diatoms, coccolithophorids, etc.) that assemble intricate bioclastic 3-D structures. For example, tens of thousands of diatom species currently exist, with each species assembling silica nanoparticles into a microshell with a distinct 3-D shape and pattern of fine features. Through sustained biological reproduction, diatoms can generate enormous numbers of 3-D micro/nanostructures with identical morphologies. Such massive parallelism and species-specific (genetically-controlled) precision are highly attractive for device manufacturing. However, natural bioclastic chemistries are rather limited. With BaSIC, synthetic approaches have been developed to convert biogenic assemblies into non-natural chemistries (e.g., TiO₂, ZrO₂, MgO, BaTiO₃, polymers, etc.), while preserving the 3-D shapes and fine (nanoscale) features. Future research on the genetic engineering of biomineralizing micro-organisms may be coupled with BaSIC to yield low-cost nanostructured devices with tailored shapes and tailored chemistries.

15-05

Preparation of Small Materials by Interface Selective Reactions Using Biological Materials as Templates

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Hydrolysis and condensation reactions of water soluble precursors of titania, alumina, silica, silsesquioxane and iron oxide were examined in the presence of interfaces of oil and water or gas and water. Hydrolyzed products from some of these precursors showed interface selectivity as inorganic materials formed selectively at the interfaces. Oil drops and air bubbles coated with silica, titania, alumina, or iron oxide were successfully prepared at room temperature. This type of reaction was applied to coat biological templates that had regular structures such as lipid tubes, hairs, gills of mushrooms, fungi, fibroblasts, and bacteria. The biological materials coated with silica, alumina and titania formed smaller and more rigid replicas of their original shapes than uncoated ones. The sizes of replicas were usually 1/10 to 1/20 of the original materials. Results indicated that most biological materials would be useful as templates to prepare regularly shaped smaller structures made of different inorganic materials.

15-06

Morphosynthesis of Complex Inorganic Forms Using Pollen Grain Templates

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Biological structures are distinguished by the extremely high precision of their self-assembly, replication and functionality, and as such provide novel platforms and templates on which to construct and organize chemical processes.

In this work, we describe an exceedingly facile method for replicating the complex surface morphology of flower and tree pollen grains, which in the case of silica produces complex colloidal materials with surface areas higher than 800m²/g. Pollen is a ubiquitous and inexpensive material with a high degree of species-specific morphological complexity. The tough outer shell (exine) of pollen grains is amenable to inorganic mineralization without consequent loss of fine structure, either as a result of geological processes, or as described here through synthetic methods. We show that high-fidelity hollow inorganic replicas of pollen grains can be achieved with both amorphous (silica) or crystalline (calcium carbonate, calcium phosphate) minerals, and demonstrate their potential applicability by post-synthetic functionalization with magnetic or metallic nanoparticles. As proof-of-concept, we also show that the biocompatible replicas can be loaded with the anti-inflammatory drug, ibuprofen, the anti-histamine, chlorpheniramine, and used as a potential drug delivery system with controlled release properties.

15-07

From Organic Supramolecular Architectures to Inorganic Nanotubes

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A diversity of supramolecular structures can be created, not only in nature but also in artificial systems, by self-assembly of designed “organic” building blocks. In contrast, creation of such diverse supramolecular structures from “inorganic” materials seems to be very difficult or nearly impossible. We have studied self-assembled superstructures of crown-appended cholesterol, cyclohexane-based, and sugar-integrated gelators in organic solvents and water. They acted as versatile gelators of organic fluids such as alcoholic and polar solvents. Crown-appended cholesterol gels showed lamellar, multi-layered vesicular, helical and nano-tubular structures. On the other hand, the sugar-based gels displayed the nano-sized bundle fiber and the double-helical fiber structures. To transcribe of these superstructures into the silica or titania, sol-gel polymerization of tetraethoxysilane (TEOS) was carried out using organogels as templates to obtain novel structure of the silica in the absence or the presence of metal ions. After calcination, crown-appended cholesterol gelators were induced single, multi-layered nano-tubular, multi-layered vesicular and the helical ribbon structures of the silica. In addition, sugar-integrated gels were created lotus-type, spherical and the double-helical nano-tubular structures of the silica. Here, I shall discuss on the self-assembled superstructures of organogelators and the transcription of these assembled structures into inorganic nanotubes.

15-08

GEPI: Genetically Engineered Polypeptides for Inorganics as Molecular Erectors in Nano- and Nanobio-technology

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Physical and chemical functions of single celled and multi-cellular organisms are carried out through recognition and sensing by a very large number (billions) of proteins through predictable and self-sustaining molecular interactions. These functions include ion or charge exchange or transport, chemical recognition and control via enzymatic reactions, material synthesis, nucleation, growth and formation. Using biology as a guide, we design, synthesize, genetically tailor and utilize short polypeptides for potential molecular erectors, linkers, bracers, and spacers, or simply as molecular sensors, in recognition, self-assembly, ordered organization, and fabrication of nanoinorganic materials and molecularly hybrid systems in nanotechnology (molecular electronics and photonics) and nanobiotechnology (bio-sensors, -assays, and -materials). Based on the fundamental principles of molecular biomimetics, i.e., molecular recognition, self-assembly, and genetic-based fabrication, and adapting combinatorial biology protocols, we can now genetically engineer polypeptides to specifically recognize inorganic surfaces and synthetic functional molecules. Once combinatorially selected and their binding experimentally characterized, combining the bioinformatics and biophysical approaches, these GEPIs can be post-selection genetic engineered to further tailor their functions to create molecular functional constructs, versatile fundamental molecular recognition elements. This presentation will review the latest developments in this rapidly developing polydisciplinary field and demonstrate practical utilizations.

15-09

Biomimicking Drug Transport Systems

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The indigenous nutrient transport systems (Biovectors) of the body such as, circulating lipoproteins, red blood cells and protein coacervates are inspiring for the synthesis of nanomaterials for delivering bioactives because of the unique surface characteristics that render them a very high biological half-life. Some of the bioinspired drug delivery systems are described as follows: Lipoprotein mimicking biovectors (LMBVs) are nanoemulsions or solid lipid nanoparticles made up of lipoprotein components or their synthetic counterparts. LMBVs are useful in delivering/targeting lipid soluble drugs. Supramolecular biovectors (SMBVs) are synthetic analogues of lipoproteins designed to deliver hydrophilic drugs. SMBVs consist of a hydrophilic nanoparticle core (for drug loading), surface-grafted with lipid and surrounded by a phospholipid monolayer. Ultrathin microcapsules prepared using layer-by-layer technique are cell-mimicking biovectors (CMBVs), which display the typical characteristics of the cell membranes such as nanometer thickness and elasticity. Different types such as pseudo-vesicles and ultrathin capsule-liposome hybrid are possible variations of CMBVs. Globular proteins are water rich structures that can be used for delivery of protein binding drugs. Globular protein mimicking biovectors (GMBVs) are nano coacervates or nanogels that are water-rich, water-

insoluble bodies due to lot of water associated with them. Biomineralized spherical inorganic nano-calcium phosphate covered with water-associated sugars, called aquasomes, are used for protein delivery. The experimental experience regarding their synthesis and pharmaceutical use shall be discussed in the presentation.

15-10

Biomimetic Polymer Networks as Functional Components in Diagnostic and Therapeutic Microdevices

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Biomimetic polymer networks with tailored affinities and transport properties for a target molecule have been developed, and these networks have been demonstrated as functional components in micro- and nanoscale diagnostic and therapeutic devices. For controlled drug delivery, these polymers can enhance control over the transport properties of therapeutic molecule and the corresponding release profile. In biosensors, these polymers are advantageous alternatives since they do not incorporate any biological components but mimic biological recognition pathways, while being more robust and cost effective. Specifically, glucose responsive copolymer networks containing poly(ethylene glycol) *n* dimethacrylate (where *n* is the number of EG repeat units) at various crosslinking percentages and acrylamide as a functional monomer were synthesized in polar, aprotic solvent (dimethyl sulfoxide). Of particular interest, methods were developed to micropattern these polymer networks with controlled thicknesses. The equilibrium binding characteristics and the kinetic binding and release characteristics of a fluorescent glucose analogue was analyzed using fluorescent microscopy techniques. Methods were developed to integrate these networks with substrates at the micro-/nanoscale, enabling the fabrication of microdevice platforms that are based on silicon technologies.

15-11

Polymorphism of DNA-Anionic Liposome Complexes Reveals Hierarchy of Ion-Mediated Interactions

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Self-assembled DNA delivery systems based on anionic lipids complexed with DNA using divalent cations have been recently introduced as an alternative to cationic lipid-DNA complexes due to their low cytotoxicity. We investigate anionic lipid-DNA (AL-DNA) complexes induced by different cations using synchrotron Small Angle X-ray Scattering (SAXS) and confocal microscopy to show how different ion-mediated interactions are expressed in the self-assembled structures and phase behavior of AL-DNA complexes. Divalent ions can mediate not just DNA-membrane attractions, but also inter-membrane and inter-DNA attractions, both absent in cationic lipid-DNA complexes. Moreover, divalent cations can coordinate non-electrostatically with lipids and modify the resultant membrane structure. We find that at low membrane charge densities, AL-DNA complexes organize into a lamellar structure of alternating DNA and membrane layers crosslinked by ions. At high membrane charge densities, a new phase with no analog in cationic lipid-DNA systems is observed: DNA is expelled from the complex, and a lamellar stack of membranes and intercalated ions is formed. For a subset of the ionic species, high ion concentrations generate an inverted hexagonal phase comprised of DNA strands

wrapped by ion-coated lipid tubes. A simple theoretical model shows that this transition is consistent with an ion-induced change in the membrane spontaneous curvature.

15-12

Directed Cell Migration via Chemoattractants Released from Degradable Microspheres

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Chemotaxis, cell migration directed by spatial concentration gradients of chemoattractant molecules, is critical for proper function of the immune system. Materials capable of generating defined chemoattractant gradients via controlled release may be useful for the design of improved vaccines and immunotherapies that draw specific cells to an immunization site. To this end, we encapsulated formyl-Nle-Leu-Phe-Nle-Tyr-Lys (fN'LFN'YK) peptides or macrophage inflammatory protein-3a (MIP-3a or CCL20) in degradable poly (lactide-co-glycolide) microspheres that provided sustained release for more than 2 weeks *in vitro*.

fN'LFN'YK and MIP-3a chemoattract dendritic cells (DCs), the key antigen-presenting cells involved in generation of primary immune responses, and their precursors, monocytes. Using an *in vitro* videomicroscopy migration assay, we detected strong chemotaxis of human monocytes and monocyte-derived DCs through 3D collagen gels toward microspheres releasing fN'LFN'YK. Similarly, microparticles releasing MIP-3a were able to attract mouse bone marrow-derived dendritic cells. Strikingly, prolonged attraction of DCs from distances up to 500 μm from the source to the point of contact with individual microspheres was observed. Such microspheres could be of general interest for the design of vaccines that promote adaptive immunity and as a platform for studying the biology of chemotaxis *in vitro* and *in vivo*.

15-13

Biomimetic Processing through a Polymer-Induced Liquid-Precursor (PILP) Process

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Studies by the biomineralization community are finding that some of the classic examples of biominerals are formed by an amorphous precursor phase. It seems reasonable to assume that this is one of the primary functions of the acidic proteins associated with biominerals because this can provide a relatively simple means of “molding” elaborate crystal morphologies, the hallmark of biominerals. However, Meldrum and coworkers have demonstrated that elaborate single-crystalline morphologies can also be molded simply by proper selection of the “mold” and crystallization conditions. If this is the case, then one must wonder why Mother Nature has apparently chosen to use the amorphous precursor route? This talk will attempt to address this question through examples taken from our *in vitro* model system, which demonstrates that the fluidity of the amorphous phase may be critical for achieving some of the morphological features found in biominerals, such as mineral fiber formation via a solution-precursor-solid (SPS) mechanism, templating single crystals via deposition of colloidal droplets, and intrafibrillar

mineralization of collagen. Therefore, our focus is not only on determining how the polymer stabilizes the amorphous phase, but also on how it entraps sufficient hydration waters to impart the amorphous precursor with fluidic character.

15-14

Aragonite Growth on Carbonate-Free Single Crystal Substrates

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Although biogenic crystals are grown under standard pressure and temperature, they often exist as metastable polymorphs. A good example is aragonite formation in seashells. Among different factors influencing the biomineralization process, much work had been done in understanding the function of impurity atoms and macromolecules. Special attention has been given to the role of lattice mismatch and stereochemistry. In this research, we tried to determine the net mismatch effect on aragonite growth, eliminating as far as possible the stereochemical contribution. For this purpose, we used several commercially available wafers free of carbonate groups, namely rhombohedral sapphire and lithium niobate, trigonal quartz and cubic silicon. All wafers were cut perpendicular to the threefold axis in order to obtain a trigonal symmetry of cations in the surface plane, which is similar to the local symmetry of Ca ions in the (001) plane of calcite and aragonite.

Experimental results [1] clearly show that aragonite can nucleate and grow *c*-oriented at mismatches up to 11%. It appears, that up to this value, the reduction of interfacial energy allowing aragonite formation prevails over the increase in the mismatch-induced strain energy. Note that we did not completely suppress the formation of calcite, but facilitated the concurrent nucleation of aragonite crystals. These findings could shed an additional light on the metastable polymorph growth in biogenic crystals.

15-15

Morphological Control of Inorganic Crystals

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One of the most immediately striking features of many biominerals is their remarkable morphologies. While many biominerals exhibiting unusual shapes and curved surfaces are amorphous in structure and therefore without a preferred morphology, many biogenic single crystals also exhibit overall morphologies which do not reflect the internal crystal structure, such as the sponge-like calcite skeletal plates of echinoderms. The research described here adopts a biomimetic approach to investigate morphological control of inorganic single crystals. Calcium carbonate has been precipitated within the confines of the regular cylindrical pores of track etch membranes, and the role of an amorphous calcium carbonate (ACC) precursor in morphological control of the product crystals was investigated. A more dramatic demonstration of the control of single crystal morphology was obtained on precipitation of a range of crystals in polymer membranes with sponge-like morphologies. Under a specific range of reagent concentrations, single crystals with sponge-like morphologies were precipitated, as dictated by the confines of the polymer membrane. These experiments demonstrate that simple shape-constraint is sufficient to produce single crystals with non-crystallographic morphologies. Patterning of the surfaces of single crystals has also been produced by precipitation of inorganic crystals on arrays of close-packed silica or polystyrene spheres.

15-16

Preparation, Characterization and Properties of Nanocrystalline Apatites: Significance for Bone Mineral and Biomaterials

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Biological poorly crystalline apatites are the main constituent of mineralized tissues (bone and dentine) but despite their widespread occurrence, the structure, properties and mode of formation of the apatite nanocrystals are still the subject of discussion. Synthetic nanocrystalline apatites can be easily prepared in aqueous media under ambient conditions. One of the most interesting characteristics of the nanocrystals, revealed by spectroscopic methods (FTIR, NMR), is the existence of a hydrated surface layer, exhibiting a very fragile structure irreversibly altered on drying, that is well developed in freshly formed precipitates. This surface layer contains labile ionic species which can be easily and rapidly exchanged with ions from the surrounding fluids. The ion mobility in the hydrated layer can be related to processes of regulation of the mineral ion concentration in body fluids and also to “crystal fusion”, often observed in bone and tooth enamel, by allowing direct crystal-crystal bonding. This process could occur in self-setting biomimetic calcium phosphate cements. Although the precise structure of the hydrated surface layer is not yet precisely known, we can take advantage of apatite nanocrystal surface reactivity to prepare biomaterials (ceramics, coatings, composites) at low temperature with preserved and adaptable bioactivity.

From Amorphous Calcium Phosphate to Artificial Implants

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Osteointegration of artificial implants for bone and tooth replacement or repair is facilitated by coating the surfaces of bioinert materials (metals, polymers) with calcium phosphates. In recent years there is growing interest in biologically inspired methods in which calcium phosphate deposition is initiated at room or physiological temperature from low concentration aqueous solutions containing inorganic ions present in human blood plasma (simulated body fluid, SBF). In order to facilitate crystal growth from these solutions, the implant surface is being modified by introducing functional groups or by first depositing amorphous calcium phosphate, ACP, which then serves as a template for subsequent crystal growth. Another important issue is the inclusion of bioactive macromolecules (drugs, growth hormones, etc.) into the coatings, which has so far been attempted by coprecipitation with the inorganic phase. However macromolecules, if present in a crystallizing solution, profoundly influence the crystallization kinetics and properties of the nascent of inorganic salts. Consequently, although coprecipitation of macromolecules is possible, the properties of the calcium phosphate coatings may be profoundly affected in the process. Apparently understanding the fundamental problems associated with nucleation and growth of calcium phosphate crystals in the presence of macromolecules is of high relevance.

In the first part of this paper we shall address this problem in a review of our recent findings on the influence of polyelectrolytes, PEs, on nucleation and growth of calcium phosphate crystals, with specific attention to ACP – crystalline phase transformation and to the properties of the nascent precipitates. It will be shown that most PEs exhibit a dual effect, i.e. any particular macromolecule may inhibit or induce crystallization, the type and intensity of the effect depending on the type, charge and solution concentration of the macromolecule.

In the second part of the lecture a new, generalized method for the production of coatings of bioinert implant materials will be described, which allows one to avoid the problem of coprecipitation altogether. The method is based on initial deposition of an organic matrix in the form of a polyelectrolyte multilayer, PE ML, and subsequent deposition of ACP particles from an aqueous suspension. The procedure is repeated several times until an organic – inorganic multilayer coating of required thickness is obtained, which is then immersed into a *metastable* calcifying solution to initiate “*in situ*” crystal growth within the organic matrix. Novel organic-inorganic nanocomposite coatings, consisting of positively or negatively charged PLL – PGA multilayers (where PLL is poly-L-lysine, PGA is poly-L- glutamic acid), and calcium phosphate deposited in the amorphous form, or crystallized “*in situ*” upon and/or within the multilayers have been prepared and characterized. Adhesion and proliferation of human osteoblast cells on selected coatings has also been determined. Mechanical and biological tests have shown that composite coatings containing “*in situ*” grown poorly crystalline apatite and final PLL-PGA-layers possess appropriate biomechanical stability with well adapted adhesion sites for cell adhesion, sufficient cell growth and cell differentiation.

The advantages of the described coatings for bioinert implant materials are obvious. The coating procedure is relatively simple and can be automatized. Both the organic matrix and the mineral

phase are prepared "*in situ*" and the growth kinetics and properties of the inorganic phase can be controlled by strict control of the experimental conditions. The coating process is not sensitive to the nature, size and topology of the substrate. Bioactive proteins (drugs, growth hormones, etc.) can be incorporated within the organic matrix without losing their bioactivity. Since the organic matrix is laid down independently of the deposition of the inorganic material, the influence of the added macromolecules on the properties of the inorganic phase can be minimized.

15-18

Exploiting Oriented Aggregation to Control Nanocrystal Size and Shape

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Oriented aggregation of nanocrystals is an important mechanism of particle growth in the solution-phase synthesis of oxide nanoparticles. Oriented aggregation is a special case of aggregation in which primary nanocrystals are aligned with respect to one another, resulting in the formation of new single crystals, often with unique morphologies. Nanocrystal growth by oriented aggregation is highly dependent on solution chemistry and may provide a means by which intricate nanostructured objects can be produced. Furthermore, surfactants can dramatically change the rate of oriented aggregation. Results from zinc oxide and iron oxide experiments will be presented.

15-19

Unusual Particle Shapes and Assembly Structures from Mineralized Hydrogel Microspheres – a Bioinspired Route to Hierarchical Structural Complexity

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Hydrogel microspheres are spherical hydrophilic polymer networks, swelling or shrinking in response to environmental variables such as pH and temperature. Thanks to their excellent biocompatibility, aqueous inner environment, and facility of conjugation with biomacromolecules, hydrogel microspheres provide appealing analogues of biological organisms, such as single cell compartments. This presentation will be focused on mineralization of CaCO_3 within hydrogel microspheres, creating inorganic/organic composite particles with unusual shapes. Various nanoparticles were incorporated into the hydrogel spheres based on their stimulus-sensitive swelling behavior. The introduction of nanoparticles enables not only adding diverse functions into the composite particles obtained but controlling their shapes also. After dip-coating on substrates, intriguingly, CaCO_3 -loaded hydrogel microspheres are organized in a two-dimensional (2D) hexagonal non-close packing array, rather different from conventional 2D colloidal crystals. The separation distance of the neighboring particles can be tuned in a controlled fashion. Reminiscent to the corneas structure of moth eyes, the resulting 2D non-close packing structures render the substrates anti-reflective, suppressing the reflection of light. Owing to their similarity to lithographic patterns, they were further recruited as templates for self-assembly of other particles. The resulting binary structures can be easily manipulated by the surface wettability.

15-20

Dendrimers and Diatoms: Bio-Inspired Routes to Functional Metal Oxides.

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Unicellular plankton known as diatoms are able to produce ornate nanostructures of silica at ambient conditions. In contrast, current materials approaches require extremes of temperature and pH. Diatoms are able to biomineralize the silica using species specific peptides known as silaffins that possess lysine residues heavily post-translationally modified with polyamines. Herein, we report the use of amine-terminated dendrimers as mimetic templates for silica condensation. Further, the unique host-guest capabilities of the dendrimer may be used to create novel functional silica nanospheres with applications in supported heterogeneous catalysis, biocatalysts, and as biological probes.

15-21

Bioinspired Nanomaterials Synthesis

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The study of the synthesis, exotic properties, assembly/packaging and potential commercial application of nanomaterials is an extremely important topic of research that is expected to have far-reaching impact global impact. The focus of my talk will be on an emerging branch of nanotechnology that derives its inspiration from biology. Recognizing that some of the most exquisite and highly functional nanomaterials are grown by biological systems (examples include silica by diatoms and magnetic nanoparticles by magnetotactic bacteria), many researchers have focused attention on understanding how inorganic materials are made by biological systems and attempting to replicate such processes in the lab. In my laboratory, we have investigated the use of plant organisms such as fungi in the synthesis of nanomaterials over a range of chemical compositions that include metals, metal sulfides and oxides. An exciting recent development is the use of plant extracts in nanoparticle synthesis wherein large concentrations of gold nanotriangles have been obtained that have potential application in cancer hyperthermia. Organisms such as fungi are not normally exposed to metal precursor stresses – that they should be capable of a broad range of biochemical transformations to negate these stresses is useful in materials chemistry and throws up exciting possibilities.

15-22

Bionanotechnology Approach in Material Synthesis and Device Fabrication by Applying Peptide/Protein Assemblies

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Non-lithographic fabrications of devices such as electronics and sensor have been studied extensively by assembling nanometer-sized building blocks into the device configurations. While various nanocomponents have been applied as building blocks to construct nanodevices, the more reproducible methods to assemble them onto precise positions are desirable. We have been fabricating peptide-based nanotubes (antibody) and functionalizing them with various recognition components (antigen), and our strategy is to use those functionalized peptide nanotubes, which can recognize and selectively bind a well-defined region on patterned substrates, as building blocks to assemble three-dimensional nanoscale architectures at uniquely defined positions and then decorate the nanotubes with various materials such as metals and quantum dots for electronics and sensor applications. This coating was obtained by incorporating certain peptide sequences into peptide nanotubes that can selectively grow specific nanocrystals on nanotubes via biomineralization. By controlling the peptide conformation on the nanotubes, the nanocrystal size, packing density, and shape were controlled. This sequence peptide-incorporated nanotube is expected to become a conductivity-tunable building block for nanodevices.

In Nature, proteins and peptides mineralize various types of metal/semiconductor nanocrystals at room temperature in ambient pressure, which are difficult to achieve in synthetic manner. For future material syntheses, the production of monodisperse nanocrystals at an ambient condition is an important technology to develop. We mimic natural biomineralization systems, and we succeeded to grow unusual nanocrystals at room temperature in ambient pressure in doughnut-shaped peptide assemblies. The peptide nano-doughnuts were self-assembled from peptides and organic salts. Nanocrystals grown inside the peptide nano-doughnuts were extracted by destroying the doughnut templates via long UV irradiation. The size of nano-doughnut can be control by pH, and therefore the size of nanocrystals can also be controlled. These nano-doughnuts can be self-assembled on specific locations of substrates patterned by AFM-based nano-lithography. Since the size and the interval between nanocrystals are controllable, these nano-doughnut assemblies can be applied to photonics and optics.

15-23

Self-Assembled Nanofibers and Tubes from Biobased Synthetic Amphiphiles

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The self-assembly of low molecular weight building blocks into nanoscale molecular objects has recently attracted considerable interest in terms of the bottom-up fabrication of nanomaterials. The building blocks currently used in supramolecular chemistry are synthesized mainly from petroleum-based starting materials. However, biobased organic synthesis presents distinct advantages for the generation of new building blocks since they are obtainable from renewable resources. This study is an effort to combine the philosophies of green chemistry and

supramolecular chemistry, making use of renewable plant-derived resources as the starting materials (an alternate feedstock) for the noncovalent synthesis of meso- and nanoscale structures. The use of cardanol (obtained from *Anacardium occidentale L*, a renewable resource and by-product of cashew industry) and its derivatives for various applications is well known. However its use in the synthesis of aryl glycolipids and their self-assembled nanostructures are new to the literature. The glycolipids are self-assembled to form a variety of well-defined nanostructures including liquid crystalline phases, nanofibers, low-molecular weight gelators and nanotubes under suitable conditions, which could be of use in material applications. Also address the synthetic strategy for new amphiphiles and advances that have led to the understanding of chiral behaviour and the subsequent ability to control the structure of glycolipid nanostructures and the resulting impact of this on future material applications.

15-24

Thermally Responsive Silica-Living Polypeptide Composite Particles.

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Core-shell composite particles have been prepared, each consisting of a silica-coated cobalt center to which a homopolypeptide shell, either poly (α -carbobenzyloxy-L-lysine) or poly (α -benzyl-L-glutamate), is attached covalently. Core particles were coated with a mixture of amino and passivating moieties through silylation reactions. The amino groups initiated the polymerization, with attachment, of *N*-carboxyanhydride monomers, resulting in a homopolypeptide shell. Characterization by dynamic light scattering confirmed the helix-coil transition of the polypeptide shell, reminiscent of the coat proteins of certain viruses, through repeated heating and cooling cycles in an organic solvent. The living nature of the polypeptide shell has also been confirmed. The particles have a size and uniformity that leads to formation of colloidal crystals. Magnetometer measurements suggest the particles are superparamagnetic. Supported by NSF.

15-25

Active Transport and Assembly Using Motor Proteins

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Energy-consuming proteins including the motor protein kinesin and the microtubule-forming protein tubulin participate in a wide range of materials transport and assembly functions in living systems. Using such “nano-robots”, organisms can create and reconfigure materials via active processes that are not limited by the diffusion and energy constraints encountered in classical self-assembly processes. We are exploring the extent to which these active proteins can be exploited in artificial microfluidic systems to transport and assemble objects ranging in size from molecules to micron-sized objects. Our ultimate goal is to mimic biological processes such as the assembly of diatom skeletons and the reconfiguration of particulate arrays in the color-changing system of the chameleon. This talk will summarize progress made to date towards

achieving this goal, including stabilization of proteins for use in artificial environments, guiding of transport, cargo manipulations (particle loading and unloading), and the generation of artificial microtubule organizing centers as scaffolds for particle manipulations.

15-26

Biomaterials from Nanocolloids: Applications for Neurons

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The presentation will review the recent advances in the use of nanocolloids to add new functionalities to biomaterials. Layer-by-layer assembly (LBL) affords preparation of ordered layered structures from virtually unlimited palette of nanocolloids. Various functionalities of nanocolloids afford preparation of targeted composites for evaluation of different neuronal functions. Four examples will be discussed. Multilayers from TiO₂ nanoshells afford selective determination of neurotransmitters due to ion-sieving effect. Strong, flexible and electroconductive implants can be made from SWNT LBL multilayers. Stringent testing of biocompatibility of these composites was undertaken and it was demonstrated that they are suitable for long-term contacts with tissues. Stimulations of neurons through these films was demonstrated. Nanoparticles with silver nanocolloids can be used to suppress inflammation processes due to infection – one of the most important problems with implantable devices. Photoactive multilayer from semiconductor particles were used to NG108*15 neuron precursor cells on them. It was found that light adsorbed in the nanoparticle layers results in the electrical excitation of the neurons making this system a functional analog of retina. Assemblies of clay-polymer systems demonstrated exceptional toughness similar to that observed in bones. Layered nanocomposites represent an exceptionally versatile tool for production of biomaterials with novel applications derived from unique properties of nanostructured matter.

15-27

Electronic Nanodevice Piggyback on Live Bacteria

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Biological motifs ranging from single biomolecule (i.e. DNA, proteins) and biomolecular monolayers (i.e., S-layer), to single-cell (bacteria, viruses, diatoms) and multi-cellular microorganisms (i.e., yeast), are shown to be highly versatile scaffolds for high density, self-assembly of nanoparticles. Leveraging the multi-scale organization in microorganism to fabricate hybrid structure with ‘physical’ nanoscale devices can open doors to fabricate highly functional (integrated) micro-systems. The key to exploiting the hierarchical structure of the microorganism to fabricate electronic micro-system remains in obtaining physiologically well-integrated biophysical hybrid structure interconnected to power and signal ports. We will discuss a fabrication method of using the membrane nanostructure of bacteria to form micron-scale (monolayer) percolating network of Au nanoparticles self-connected to power/signal ports. Using the humidity-induced actuation characteristics of the bacterium to modulate the (single) electron tunneling characteristics of the nanoparticle monolayer we demonstrate, a reversible and robust, humidity-sensing device. A critical aspect that attributes to a successful device is that the bacteria are alive during the entire device fabrication process. In contrast to most impedance

based microelectronic humidity sensors, the sensitivity of this device is best at low humidity (relative humidity <20%).

15-28

Spontaneous Assembly of Macroporous Titania

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Titania is a multifunctional material with a wide variety of potential uses in diverse areas such as photocatalysis and bioactivity. There is considerable interest in the template-directed synthesis of porous titania as the increased surface area and chemical accessibility of such materials offers distinct advantages. Typically, porogens with well defined size and architecture, such as emulsion droplets and colloidal crystals have been used in combination with preformed nanoparticles or in-situ precipitation reactions to prepare macroporous ceramics. In this work, we demonstrate the spontaneous formation of ordered macroporous titania from base catalysed sol-gel reactions and describe the photocatalytic properties of these materials.

15-29

Biotechnology and Biomimetics Opens New Routes to the Fabrication of Silica and Metal Oxide Semiconductors

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Working with silica needles produced by marine sponges, our laboratory discovered that the proteins we named “silicateins” catalyze and structurally direct the hydrolysis and polycondensation of silica, titania, gallia and zinc oxide from alkoxide precursors at neutral pH and low temperature. The silicateins are true enzymes, closely related to a well-known family of hydrolases. These are the first reported examples of enzyme-catalyzed, nanostructure-directed synthesis of these materials – and the first such syntheses at low temperature and neutral pH. Interaction with the template-like protein surface is capable of stabilizing polymorphs of these materials that otherwise are not normally observed at low temperatures. A preferential alignment of the resulting nanocrystallites of gallia to the protein was recognized, suggesting an epitaxial-like relationship.

Biomimicry is currently being used to catalyze and template the growth of various metal oxides. We are incorporating analogs of the critical amino acid residues found in silicatein’s catalytic active site, anchoring these functional groups (via self-assembled monolayers on gold) adjacent to one another to facilitate catalytic activity by the same mechanism exhibited by the enzyme. Results have shown that biomimetics of the active site in silicatein are capable of producing silica and metal oxides from alkoxide precursors at neutral pH.

15-30

Surface Patterning of Silica Nanostructures Using Bio-Inspired Templates and Directed Synthesis

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Natural systems excel in directing the synthesis of inorganic materials for various functional purposes. One of the best-studied systems is silica synthesis. Various biological and synthetic polymers have been shown to template and catalyze silica formation from silicic acid precursors. We will describe the use of poly-L-lysine to promote the synthesis of silica in neutral, aqueous solution and when immobilized onto a silicon support structure under similar conditions. Either reagent jetting or conventional photolithography techniques can be used to pattern the templating polymer. Highly interconnected laminate structures are created after exposure to dilute solutions of silicic acid. Photolithographic patterning of (3-aminopropyl) trimethoxysilane, a reagent that mimics the lysine functional group, led to similar silica coatings. The described surface patterning techniques offer a route to integrate conventional silicon patterning technologies with biologically based material synthesis. Such combined fabrication techniques enable controlled assembly over multiple length scales and an approach to understanding interfacial silica synthesis as occurs in natural systems.

15-31

Biomaterials with Hierarchically Defined Micro- and Nano-Scale Structure

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Biomaterials are becoming increasingly important in biomedical practice, particularly as the population ages. Materials that are organized on multiple length scales bear a closer resemblance to biological matrices than those with single scale features and materials with multi-scale organization should be more advantageous in biomedical applications. Many studies have shown that both the micrometer- and nanometer-scale features of materials could significantly influence cellular responses, however, synthesis of organized structures with both length scales for direct biomedical applications has been lacking. Nature has presented us numerous clues on how to produce complex, organized structures. Using a hierarchical approach that mimics natural material formation processes, we developed a method to produce materials with controlled physical structures at both the micrometer and nanometer scale. Our method is based upon a pre-organized micropatterned template and conformal transformation of the architecture with nano-structured minerals, namely hydroxyapatite. The newly developed materials were biocompatible with bone cells, induced a range of desirable cellular responses, and may therefore have direct application in bone tissue engineering. In addition, the design principles employed in this study can be extrapolated to other classes of biomedical materials, including polymers, metals, ceramics or hybrid combinations.