SYMPOSIUM GG
Mesoscale Architectures from Nano-Units—Assembly, Fabrication, and Properties

November 29 - December 2, 2004

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* Invited paper
Ligand coated metal nanoparticles are promising nanomaterials for novel electronic and optical devices. Their main strength is in the fact that they combine the advantages of small metals, such as single electron transistor (SET) behavior, together with most of the advantages of the organic ligands that are used to coat them, such as solubility in organic solvents and processability for example via self-assembly methods. Moreover, even complex nanoparticles coated with multiple types of ligands can be synthesized in just one step. Here we present a new family of mixed ligand nanoparticles that shows sub-nanometer patterns (e.g. ridges) on their ligand shell [1]. This unique sub-nano-structuring of their ligand shell provides new properties to the particles. In particular, we focus on silver and gold particles that have ridges composed of hydrophilic valleys and hydrophobic peaks. For the first time we show the ability to control the supramolecular ordering of the ligands on the nanoparticle surfaces. Independently of the mixture of ligands introduced during nanoparticle synthesis, one can control the resulting surface properties of the nanoparticles. Scanning tunneling microscopy images show ridges 3 Å and 8 Å wide on the ligand shell of nanoparticles. The shape and size of both of these parameters is provided by the choice of the ligands and of their molar ratio respectively. We also demonstrate that the nanoparticle ligands interact so as to align the stripes of neighboring nanoparticles over large length scales. The synthetic approach that leads to the formation of this supramolecular ordering will be discussed. These particles show unique and unexpected self-assembly and surface chemistry properties, in particular they show a remarkable resistance to protein adsorption. 1. A. Jackson, J. Myerson, and F. Stellacci, Nature Materials 2004, 3, 330

Directed Assembly of Metal-Organic Nanoarchitectures. Klaus Kern, 1 Nanoscale Science Department, Max Planck Institute for Solid State Research, Stuttgart, Germany; 2 Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland

We developed a novel method for preparation of asymmetrically coated colloid particles by using a microcontact printing technique. First, water-insoluble ionic dyes are deposited onto polyelectrolyte stamps which were printed onto latex particle monolayers of opposite surface charge in order to produce spherical latex particles of dipolar charge distribution. We studied the effects of salt on the aggregation of such dipolar particles in aqueous suspensions. Upon addition of salt, dipolar colloid particles were found to give linear aggregates. We have also extended this microcontact printing technique to the directed assembly of colloidal particles. Microcontact printing of one colloidal monolayer over a latex particle monolayer of opposite charge was used to fabricate particles of complex internal structure. We demonstrated that if the two colloid monolayers consist of particles of comparable sizes, this method allows fabrication of asymmetric particle doublets. When the particle monolayer was stamped with another colloid monolayer of much smaller particle size, complex structures such as half-coated raspberry-like particles were obtained. Possible applications of these asymmetrically coated colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids.

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silica films with an array of oriented and accessible cylindrical pores. The process is rapid, efficient and easily extendable to other metal oxides. 1. Hui et al., Science 2004, 303, 507.

10:45 AM GG1.7 Patterning Complex Multi-Component Structures with Ferroelectric Nanolithography. Deworn Benneil, Xiaojun Lei and Dongbo Li; Materials Science, University of Pennsylvania, Philadelphia, Pennsylvania.

Complex structures are fabricated by independently locating multiple nanostructures in pre-determined positions, overcoming one of the limitations of self-assembly in a process that operates on multiple types of compounds simultaneously. Atomic polarization in ferroelectric perovskites is manipulated to control surface electronic structure and local chemical reactivity. Paradigm for ferroelectric domain patterning using scanning probe microscopy, electron beam lithography and microcontact stamping are presented. Photo reaction of inert and normally non-functionalized porphyrins and peptides, and semiconductor nanoparticle allows assembly into configurations that yield nanodevices, such as optoelectronic switches and modulators. Sequential and simultaneous patterning of multiple compounds will be demonstrated.

11:00 AM GG1.8 Directed Crystallization of Functionalized Molecules on Nanopatterned Self-Assembled Monolayers. Ashok Kakkar, Florence Quist and Adam Dickie; Chemistry, McGill University, Montreal, Quebec, Canada.

Surface chemistry offers a unique opportunity to assemble desired molecules into organized and controlled architectures that can imitate crystallization in molecular recognition. Such a methodology offers tremendous potential in addressing key issues related to controlled polymorphism in pharmaceutical solids and construction of smart materials. We have recently developed a serial templating methodology to construct patterned nanostructures on semiconductor substrates. These self-assembled thin films can direct nucleation and crystal growth of functionalized molecules using a combination of molecular recognition and supramolecular interactions. The resulting solid state materials can be easily tailored by subtle variations in self-assembling patterning components. A detailed examination of combining bottom-up chemisorption process with supramolecular association in controlling polymorphism in solids will be presented.


In solution stamping nano-lithography (SSNL), an elastomeric stamp containing relief pattern is manually manipulated to contact surface solution of inorganic (functional oxide or ceramic) materials, and then placed on a surface to transfer this "ink" from the stamp to the substrate. Due to the flexible mechanical properties of the elastomeric material, the stamp forms a conformal contact with the surface. Ink transfer only occurs at locations where the stamp contacts the surface, because of the stamp morphology. Hence, the resulting patterns on the substrate mirror the stamp relief structures. The stumped precursor pattern is converted following standard procedures to convert them to the final composition of the inorganic materials. If a lattice-matched substrate is used, the patterned thin films may be epitaxially registered to the substrate. Epitaxial deposition of 100nm thick superconducting YBCO films has been demonstrated with this method to date. Research in pushing lateral resolution downward toward 200nm will be reported. In addition, initial work toward combination function and top-down patterned self-assembly of nanoparticle has been discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:30 AM *GG1.10 Fabrication of 3D Nanoarchitectures by Way of Nanocopying of Natural Substances. Copying of DNA Strand and Artificial Possibilities. Toshiyuki Kunitake1,2, Shigeki Fujisawa2, Rie Tokaki1 and Jianguo Huang1; Frontier Research System, RIKEN, Wako, Saitama, Japan; 2The University of Kitakyushu, Kitakyushu, Fukuoka, Japan. 

We define nanocopying as "copying of nanometer-size objects such as molecules, supermolecules, nano-particles and surface morphologies with nanometer precision"(1). There are two types of copies - positive copy and negative copy. Positive copy with the nanometer precision should be achieved by using a given template with ultrathin (nanometer-thick) layers. Subsequent template removal. In contrast, negative copy is formed as a result of stamping and void filling (molding). It is also obtained by embedding/removal of molecular templates in copying matrices. Formation of negative copy is a typical case of negative copy. In order to achieve nanometer precision, the matrix material has to be uniform, shape-adaptable at the nanometer precision, and self-supporting. The former property is essential for recreating morphological characteristics of the copied object. Infinite amorphous solids such as organic polymers, inorganic glasses and metals may be candidate materials for this purpose. Certain metals may produce ultrathin layers with complex morphological characteristics of templates. However, metal nanosheets and polymer nano-layers are probably not robust enough for sustaining 3D structures of nano-sized copies. The surface sol-gel process can satisfy the above requirements of the copying matrix. We applied this method to natural substances. Cellulose fibers possess surface hydroxy groups, and filter paper provides a suitable vehicle for the process. Upon removal of the template paper, the overall shape of the original filter paper is well preserved except for a scale shrinkage in size, and the original morphology of the intertwined fibers was faithfully replicated by titania nanotubes(2). As another example, we conducted nanocopying of DNA strands (3). Lambda DNA molecules were spread on a solid substrate, and subjected to the surface sol-gel process with titanium butoxide. The occluded DNA chains cannot be decomposed by DNase and can be removed by oxygen plasma. The resulting nanotubes were clearly observed by TEM. (1) S. Fujikawa, T. Kunitake, Analytical Chemistry, 75(2003), 1-6 (2) J. Huang, T. Kunitake, J. Am. Chern. Soc., 125(2003), pp. 11834-11835 (3) R. Takaki, S. Fujikawa, T. Kunitake, in preparation

SESSION GG2: Nanotemplating for Meso-scale Self-Assembly II

Chairs: Paul Braun and Mauricio Terrones

Monday Afternoon, November 29, 2004 Room 311 (Hynes)

1:30 PM *GG2.1 Controlling Emerging Nanoscale Structure in Materials Synthesis. Yiyung Wu1, Guosheng Cheng2, Kirill Katsov3, Scott W. Sides4, Jianfang Wang1, Jing Yang1, Glenn H. Fredrickson1,3, Martin Moskovits1 and Galen D. Stucky2; 1Dept of Chemistry & Biochemistry, UCSB, Santa Barbara, California; 2Materials Dept, UCSD, Santa Barbara, California; 3Dept of Chemical Engineering, UCSB, Santa Barbara, California.

A fundamental pursuit in materials science is control of molecular assembly by changing the synthesis environment without modification of the precursor chemistry or other reaction conditions. In a physically confined environment, interfacial interactions, symmetry breaking, structural frustration, and confinement-induced entropy loss play dominant roles in determining molecular organization. This talk will illustrate the concept of emergent structures with results on confining the assembly of silica-surfactant composite mesostructures inside cylindrical alumina nanochannels. Varying the diameter of the nanochannels spontaneously produces a variety of architectures, including unprecedented chiral silica mesostructures with single-helix and double-helix geometries. Upon tightening the confinement, a transition occurs in the mesopore morphology from a cylindrical to a spherical cage-like geometry. Additional nanoscale sculpted configurations are accessible by modifying the confinement constraint. The e-mesostructures produced by confined synthesis can be used for the creation of functionalized high pore density membranes and as templates for fabricating highly ordered mesoscaled nanowires and nanowire periodic arrays with metallic or semiconducting functionality.

2:00 PM GG2.2 Mesostructure Control of 1D Mesoporous Silica within Anodized Alumina Membranes. Hong Kou1, Donghai Wang2, Zhenzhong Yang2 and Yunfeng Lu4; 1Chemical and Biomolecular Engineering, Tulane university, New Orleans, Louisiana; 2State Key Laboratory of Polymer Physics and Chemistry Joint Laboratory of Polymer Science and Materials,Institute of Chemistry, Chinese Academy of Science, Beijing, China.

Cooperative self-assembly of silicate and surfactant can generate liquid crystal structured mesophases (e.g., hexagonal, lamellar or cubic structure), thus forming highly ordered mesoporous silica after removal of surfactants. Due to the unique mesoscale structures, various morphologies, and controllable surface properties, mesostructured silica or composite materials have been applied in microfluidic devices as catalysis, separation, sensor, optical materials, templates synthesis, etc. It is increasingly important to control mesoporous materials in a small feature such as micro/nano scale size for its potential device applications. In this work, we have
investigated the self-assembly behavior of silicate/surfactant confined within hydrophilic anodized alumina membrane and obtained 1D mesoporous silica with a variety of mesostructures distinct from both bulk and previously reported 1D mesoporous materials. With increasing surfactant concentration in the precursor solution, mesostructures of 1D mesoporous silica were changed from disorder, cubic, spiral hexagonal to circular lamellar structure. As the size of mesophase is down to nanoscale, interfacial property also plays prominent roles on the self-assembly behavior of silicate/surfactant. Liquid-solid interface at the pore surface serves as a nucleating surface for inward growth of silicate/surfactant mesophase radially till the pores are completely filled. The circular curvature of nucleating surface result in circular growth of hexagonal or lamellar liquid crystalline mesophase, and therein forming the corresponding spiral hexagonal and co-central lamellar structured 1D mesoporous silica. With incorporation of shearing field in growth of mesophase within alumina pore channels, straight hexagonal mesoporous structure perpendicular to the membrane plane were achieved. This research will bring the hole in nanoscale confinement effect to cooperative inorganic-organic self-assembly behavior. We expect that this new unique structured mesoporous silica arrays will be applicable to templated synthesis, separation and other applications.

SESSION GG3/C2: Joint Session: Emerging Paradigms in Nanopatterning and Mesoscale Assembly

Chair: Paul Braun, Eric Lu and G. Ramanath

Monday Afternoon, November 30, 2004
Room 311 (Hynes)

2:30 PM *GG3.1/C2.1
Mesoscale Architectures from Nanounits: Assembly, Fabrication, A. Paul Alivisatos, Chemistry, University of California, Berkeley, Berkeley, California.

This talk will focus on the use of creation of new shapes and topologies of nanocrystals. Nanocrystals can act as a fundamental unit for chemical transformation. For example, through studies of interdiffusion between two components in a particle, we have learned how to make hollow inorganic nanocrystals. A second example concerns controlled branching, which enables us to create new types of heterostructures, a very recent work in which we employ cation exchange to alter the chemical composition of nanocrystals will be described.

3:00 PM *GG3.2/C2.2

The rapid rise of the semiconductor industry is without doubt one of the main success stories of modern industrial development. At the heart of the industry's success is its ability to keep shrinking device sizes exponentially over time according to Moore's Law, resulting in ever decreasing cost per function. As of today, the industry's Roadmap looks out 14 years, until 2018, without forecasting a slowdown of Moore's Law. From the technical side, we have a pretty good understanding of what needs to be done to pattern the 45 nm nodes. The Roadmap requires at the end of this decade, but there are still fundamental questions to be resolved for the years further out. In particular, some question whether the patterning capability of the chemical amplification mechanism (which underlies the dominant class of photolithograhic today) can be extended beyond 59 nm. Even if the technical hurdles are overcome, the investment cost of photolithography and manufacturing future chip generations in general may become so high that the market will be unable to bear it. Such an economic end to Moore's Law could occur even if it is technically feasible to make smaller devices and although the cost per function would continue to decrease. Following an outline of present and future semiconductor technology, this paper will explore a way out of the coming crisis that may lie in the use of some form of nanoimprint technology, which presently still in an early stage but has the potential to be substantially cheaper than conventional photolithography.

3:30 PM *GG3.3/C2.3
Unconventional Nanofabrication and Mesoscale Self-Assembly, George M. Whitesides, Logan McCarty, Qiaobing Xu, Byron Gates, Hangyuan, Lara Estase and Vijayaraman Krishnamurthy, Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts.

Chemistry, with stimulus from biology, is beginning to develop a range of new concepts for the fabrication of mesoscale systems by templated self-assembly from nanoscale components: these include a range of types of self-assembly, printing, molding, microfluidic patterning, electrochemistry, sectioning, and related techniques designed to make it possible to design complexed structures having electrical, optical, biological, magnetic functionality and to assemble and replicate these systems efficiently. These concepts suggest approaches to fabrication that are substantially different from photolithography in their areas of application.

4:00 PM *GG3.4/C2.4
Massively Parallel Dip Pen Nanolithography, Chad A. Mirkin, Chemistry, Northwestern University, Evanston, Illinois.

Dip-Pen Nanolithography (DPN) is a scanning-probe technique that permits the chemical functionalization of surfaces with nanoscale precision. Based upon a conventional Atomic Force Microscope, DPN combines ambient operation and resolutions superior to those of e-beam lithography, and allows one to create combinatorial libraries of soft matter nanostructures that can be used in fundamental surface science studies, biological diagnostics, and organic electronics. This talk will describe the fundamental capabilities of DPN and its use to generate and study a wide variety of nanostructures using materials ranging from oligonucleotides to proteins to conjugated polymers. Moreover, recent efforts to transform DPN into a high throughput tool through the use of 1 million pen cantilever arrays will be presented.

4:30 PM *GG3.5/C2.5
Nanoimprint Lithography (NIL), Laser-Assisted Direct Imprint (LADI) And Lithographically-Induced Self-Assembly (LISA), Stephen Y. Chou, Department of Electrical Engineering, Nanostructure Laboratory, Princeton University, Princeton, New Jersey.

The talk will present several innovative nanopatterning methods and their advancements developed at NanoStructure Lab at Princeton. The first is nanoimprint lithography (NIL), which patterns a resist by physical deformation using a mold. We will present our demonstration of sub-12 nm pitch, sub-5nm future size, sub-20 nm alignment (one sigma), and large-area uniformity in NIL, as well as various NIL tools. The second is laser-assisted direct imprint (LADI), which directly pattern nanomaterials on hard material surface, chemical-free and without etching. LADI uses an excimer laser, shining through a transparent mold, to melt a thin surface layer of a hard material, and then press a mold into the molten material. We will show our recent advances in sub-10 nm feature sizes. LAI stamping in SiC and metals (Au and Cu), and new applications of LADI in wafer planarization. Finally, we will present lithographically-induced self-assembly (LISA), where self-assembly of nanomaterials are guided by much large patterns and can achieve single domain over a large area. Furthermore, we used LISA to achieve self-alignments and self-assembly (SALSA) between the connections and electronic devices to create random access electronic devices array. The work was supported in part by DARPA and ONR. The author acknowledges the contributions of other members of NanoStructure Lab at Princeton to the presentation materials.

SESSION GG4: Bioinspired Synthesis, Templating and Assembly

Chair: Paul Braun

Tuesday Morning, November 30, 2004
Room 311 (Hynes)

8:30 AM **GG4.1
New methods for the synthesis of nanomaterials, Murali Sastry, Materials Chemistry Division, National Chemical Laboratory, Pune, India.

Wet-chemical methods for the synthesis of nanomaterials are extremely popular for a variety of reasons. Nanoparticles over a range of chemical compositions, sizes and shapes can be routinely synthesized in both aqueous and non-polar organic solutions with a variety of surface modifiers that include standard surfactants and biomolecules. However, many processes for nanoparticle synthesis often involve the use of toxic chemicals, which are increasingly becoming taboo. Realizing that some of the most exquisite inorganic nanostructures are synthesized by biological systems such as diatoms and bacteria, nanoscience researchers are turning towards biology for inspiration. In the first part of the talk, I will cover the work carried out in my laboratory on the use of fungi, actinomycetes and extracts from various plant parts in the synthesis of nanoparticles of different compositions. We have been successful in synthesizing nanoscale metals, sulphides and oxides by appropriate choice of microorganisms and examples will be given to illustrate this new approach [1]. While achieving tolerable nanoparticle polydispersity continues to be an important issue with biological nanoparticle synthesis methods, shape modulation may be one aspect
where select biological methods appear to be superior to chemical synthesis methods. Bubbles have fascinated man for a very long time. In the second part of my talk, I will show that liquid foams (a dense assembly of bubbles) may be used for the synthesis of nanoparticles over a range of chemical compositions. This is accomplished by ion entrapment in the foam followed by chemical reaction resulting in the formation of nanoparticles in the foam. A very complex structure and present nanoscale reactors of variable geometry that may be used creatively in the synthesis of nanoparticles of different shapes. An important advantage of the foam-based method is that it could be of value for commercial scale production of nanomaterials. [1] M. Sastry, A. Ahmad, M.I. Khan, R. Kumar, ‘Microbial Nanoparticle Production’ in Nano-in-Technology: Concepts, Applications and Perspectives (ed. C.M. Niemeyer, C. Mirkin, C. Wu, VCH, Weinheim, 2004). [2] S. Mandal, S.K. Arumugham, S.D. Adyanthaya, R. Parshra, M. Sastry, J. Mater. Chem. 2004, 14, 43.

9:00 AM *GG4.2
Genetic Approaches to Material Assembly, Stanley Brown, Dept. of Mol. Cell Biology, University of Copenhagen, Copenhagen, Denmark

Proteins play amazingly diverse structural and catalytic roles in biological systems. We wish to explore the mechanisms by which proteins can perform similar functions in the formation and assembly of inorganic materials. We have instituted an approach based on cell-surface display to investigate these mechanisms. In a strategy similar to phage display, we express random polypeptides on the surface binding energy (in the absence of solvent) of all the amino species. Calculations show that these amino acids have the strongest interactions typical of proteins and other biomolecules. First, we have found polypeptides that distinguish surfaces of identical atomic composition but different spatial orientation. Second, the polypeptides we have found that modulate gold crystal formation and dissolution utilize common proteinic mechanisms. We imagine the diverse adhesive, structural, reactive and catalytic traits of proteins can provide new solutions to technological problems.

9:30 AM *GG4.3

We have developed bio-inspired strategies for controlling the assembly of one and two-dimensional quantum dot (QD) arrays, either on substrates or as free entities in solution. Regular structures, with inter-QD distances small enough to facilitate energy transfer, have been created using the natural substrate-binding and self-assembly properties displayed by certain proteins. A detailed understanding of the interaction of amino acids with the surface of QDs was essential for this work. Studies have shown that natural and modified amino acids can bind to the surface of CdSe/ZnS (core-shell) QDs. Amino acids not only confer water solubility to QDs, but studies of these interactions also offer insights into the most suitable linkers for binding proteins and polypeptides to the QD ZnS surface. We have specifically investigated the three most nucleophilic amino acids: cysteine, lysine, and histidine, containing thiol, primary amine, and imidazole groups, respectively. Using steady-state and time-resolved photoluminescence (PL) spectroscopy, we have studied the efficiency with which the amino acids bind to the QD surface, the stability of the water-soluble product, and the ability of the group to passivate QD surface states. Both lysine and histidine were found to produce aqueous colloidal QD solutions with PL quantum efficiencies comparable to the standard tri-octyl phosphine oxide (TOPO)-capped species. Calculations show that these amino acids have the strongest surface binding energy (in the absence of solvent) of all the amino acids tested. Whereas stable histidine conjugates form readily in neutral pH conditions, strongly basic conditions are required for the preparation of lysine conjugates, which precludes the use of lysine to link QDs to proteins that denature under such conditions. Cysteine was also able to bind to QDs and produce metastable solutions at near-neutral pH conditions; however, this occurred too quickly for the analysis of the resulting proteins. Cysteine, a disulfide-containing compound, is a poor ligand and caused QD precipitation. Oxidation was successfully inhibited with dithiothreitol or by using non-natural cysteine derivatives. The use of these amino acid conjugates has enabled us to direct the interaction of QDs with proteins in a number of novel ways. The amino acid ligand can be biotinylated and incubated with avidin-containing proteins to form an irreversibly bound QD. Alternatively, genetically modified interaction of the N- and C-termini of self-assembling proteins with suitably nucleophilic polypeptide chains can facilitate a more selective binding of proteins directly to the QD surface. We present PL data and striking microscopy approaches afford excellent control over the construction of QD arrays or chains.

9:45 AM *GG4.4

As integrated circuit (IC) features continue to decrease in size and pitch the performance of conventional materials for on-chip interconnects may be severely limited by fundamental physical processes. An example includes increased resistivity of metal lines due to surface scattering at feature dimensions below the electron mean free path (~40 nm for Cu). Future nanoscale interconnect candidates may need to exploit novel conduction mechanisms such as ballast electron transport requiring a high degree of intra-molecular order. This highlights the need for such nanoscale interconnects to exploit the phenomenon of self-assembly. Self-assembly of interconnect materials may also aid in the ability to recover individuals displaying red properties from initial populations comprising millions or billions of different members. The recovery of rare individuals results from the observation that a polypeptide adhering to the selected surface allows adheres to an avidin-containing protein layer, expressing the selected amino acids tested. Whereas stable histidine conjugates form readily in neutral pH conditions, strongly basic conditions are required for the preparation of lysine conjugates, which precludes the use of lysine to link QDs to proteins that denature under such conditions. Cysteine was also able to bind to QDs and produce metastable solutions at near-neutral pH conditions; however, this occurred too quickly for the analysis of the resulting proteins. Cysteine, a disulfide-containing compound, is a poor ligand and caused QD precipitation. Oxidation was successfully inhibited with dithiothreitol or by using non-natural cysteine derivatives. The use of these amino acid conjugates has enabled us to direct the interaction of QDs with proteins in a number of novel ways. The amino acid ligand can be biotinylated and incubated with avidin-containing proteins to form an irreversibly bound QD. Alternatively, genetically modified interaction of the N- and C-termini of self-assembling proteins with suitably nucleophilic polypeptide chains can facilitate a more selective binding of proteins directly to the QD surface. We present PL data and striking microscopy approaches afford excellent control over the construction of QD arrays or chains.

10:00 AM *GG4.5
Hierarchical Self-Assembly Through Electrostatic Interactions, Gerard Wong, Materials Science & Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois; 2Physics, University of Illinois at Urbana Champaign, Urbana, Illinois.

Charged biological macromolecules of varying complexity (such as membranes, polyelectrolytes, and globular proteins) can be collectively organized through the interplay of electrostatics and entropy. These interactions are quite general, since all nucleic acids, all cell membranes, as well as most proteins and sugars are charged. Through interactions which self-assemble into macroscopic objects, frequently oppositely-charged, but in contrast to intuition, they can be like-charged as well. We will focus the discussion specifically on our recent work on interactions between charged biopolymers and charged membranes. Early examples include complexes of anionic DNA and cationic lipids for non-viral gene therapy. We have examined the general assembly of such complexes by investigating other forms of anionic biopolymer-cationic membrane assembly comprised of biopolymers of different charge, flexibility, and density. Assemblies of like-charged cationic biopolymer-membrane complexes can also be formed into like-charged biopolymers and membranes, using interactions mediated through small molecule cations. Finally, we show that molecular details of DNA can be imprinted onto CdS nanorods using biopolymer-membrane complexes.

10:15 AM *GG4.6
Biomolecular Nano lithography: Scaffold Approaches to Organized Nanoparticle Structures, James B. Hutchinson, Gerd H.
The ability to pattern nanometer-scale structures through convenient, highly-parallel processes is an important challenge in nanoscience. For electronic and optical applications of nanostructures in nanoelectronics, nanophotonics, and spintronics, the ability to precisely control the feature sizes and the spacing between the individual features at the nanometer- or Angstrom-level is necessary in order to manipulate the electronic and optical interactions (e.g. tunneling barrier height, carrier coupling, wavefunction overlap) between neighboring structures and thus tune device function and properties. In addition, the integration of these patterns into hierarchical structures that provide useful interfaces to the macroscopic world is important. Our approach is based upon functional group-directed assembly of well-defined nanoparticle building blocks. Using this approach we are pursuing 1-, 2- and 3-dimensional structures derived from gold nanoparticles. In this presentation, we will focus primarily on our efforts to organize ligand-stabilized gold nanoparticles onto DNA templates to form extended 1- and 2-dimensional assemblies. One of the key features of scaffolding approaches that rely on DNA templates is the precision with which the 2- and 3-D structures can be controlled. In addition to particle size and interparticle spacing, the pattern and size of the assembly can also be controlled. The spacing between neighboring nanoparticles can be tuned at the molecular level by utilizing nanoparticles possessing ligand shells of varying thickness to achieve Angstrom-level resolution at spacings of 1.5, 2.1, and 2.8 nm. The length of the resulting monodisperse nanoparticle polymers can be controlled precisely through choice of the DNA template (e.g. using monodisperse DNA samples comprised of 250 base pairs (~85 nm) or 500 base pairs). The subsequent assembly of these chains into extended, two-dimensional superlattices on surfaces provides a striking demonstration of how the monodisperse nature of the nanoparticle chains influences the properties of the material. The use of specifically-defined DNA templates to interface the nanoparticle assemblies for electrical characterization will also be discussed.

11:15 AM GG4.7 Assembly of Virus on Nanometric Chemical Patterns. Chun Lin Cheung1, Raymond Friddle2, Melinda Tonks3, Raymond Noy4, Julio Camarero5, Jim De Yoreo6, Anju Chatterji7, Tianwei Lin8 and John E. Johnson9. 1Biosafety and NanoSciences Laboratory, Lawrence Livermore National Laboratory, Livermore, California; 2Molecular Biology, The Scripps Research Institute, La Jolla, California.

One of the challenges associated with assembly of nanoscale elements into mesoscale structures is to develop a fundamental understanding of the physical principles underlying assembly, particularly in solvent-based systems where solvent and/or ionic bonding are of little significance and hydrophobic forces are more important. Because viruses can be genetically manipulated to select for specific materials, recent attention has been given to their use as vehicles for assembly. The ability to pattern nanometer-scale structures that provide useful interfaces to the macroscopic world is important. Our approach is based upon functional group-directed assembly of DNA templates to form extended 1- and 2-dimensional assemblies. One of the key features of scaffolding approaches that rely on DNA templates is the precision with which the 2- and 3-D structures can be controlled. In addition to particle size and interparticle spacing, the pattern and size of the assembly can also be controlled. The spacing between neighboring nanoparticles can be tuned at the molecular level by utilizing nanoparticles possessing ligand shells of varying thickness to achieve Angstrom-level resolution at spacings of 1.5, 2.1, and 2.8 nm. The length of the resulting monodisperse nanoparticle polymers can be controlled precisely through choice of the DNA template (e.g. using monodisperse DNA samples comprised of 250 base pairs (~85 nm) or 500 base pairs). The subsequent assembly of these chains into extended, two-dimensional superlattices on surfaces provides a striking demonstration of how the monodisperse nature of the nanoparticle chains influences the properties of the material. The use of specifically-defined DNA templates to interface the nanoparticle assemblies for electrical characterization will also be discussed.

11:30 AM GG4.8 Directed Assembly of Nanomaterials Based on Analyte-Specific DNAzymes. Yi Lu and Juewen Liu; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

A grand challenge in nanoscale science and engineering is how to transform self-assembly of simple structures into directed assembly of highly defined complex mesostructures. Introducing biomolecules into nanostructures provide an opportunity to meet such a challenge, as the biomolecules can be programmed to turn on and off the assembly with high speed and under constant temperature and pressure. DNAzymes, or catalytic DNA molecules, are ideal choices for directed assembly of nanomaterials, as they are consist of DNA that can be programmable genetically and possess enzymatic functions. In particular, specific DNAzymes have been used to control the growth of gold nanoparticles in which the assembly state is highly dependent on the presence of specific nucleotides such as P2+ or adenosine. The nanomaterials assembly states can be turned on or off. And the degree of assembly can also be controlled by careful use of DNAzymes with different sequences and activities. In addition to advancing directed assembly of nanomaterials, the resulting system has been used as highly sensitive and selective colorimetric biosensors for metal ions and organic molecules. The methodology is generally applicable to almost any chosen analytes and thus significantly expands its impact in both nanotechnology and other fields and technologies.

11:45 AM GG4.9 Self-assembly between DNA and anionic membranes. Hongjun Liang1, Thomas Angelini2 and Gerard C.L. Wong2,3; 1Dept. of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 2Dept. of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We investigate the structure and interactions between anionic polyelectrolytes and anionic membranes, using self-assembled complexes between DNA and anionic membranes. Like-charged DNA and anionic membrane generally repel each other, but in the presence of divalent ions, they can self assemble into complexes with a rich polydisperse nature of charges. We have demonstrated the use of DNAzymes with specific functions to control the assembly state of the complexes. In particular, the DNAzymes can be modulated the virus-surface binding strength by additions of competing metal coordinating ligands such as imidazoles. To explore the effect of virus' mobility on assembly, we varied the properties of the DNA template (e.g. concentration, number of condensed ions). Preliminary results on the phase diagram of this system and its potential applications will be discussed.

SESSION GG5: Nanowire and Nanotube Assembly

Chairs: Xavier Blase and Mauricio Terrones Tuesday Afternoon, November 30, 2004 Room 311 (Hynes)

1:30 PM *GG5.1 Fabrication of Complex Carbon Nanotube Architectures. Pulickel M. Ajayan, Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

The talk will focus on the recent developments in our laboratory on the fabrication of carbon nanotube based architectures tailored for various applications. Various organized architectures can be fabricated using relatively simple processes and some of these structures can be used for novel applications such as sensors, adhesive coatings, filters and polymer based thin film composites. Complex 2-D and 3-D structures can be controllably built from nanotube units. Our efforts on the strategies of growth and manipulation of nanotube-based structures will be discussed.

2:00 PM GG5.2 Monolayers of multivalent carbon nanotubes. Vladimir A. Samulov1, Jean Galibert2, E. Couteau3, M. Seo3, L. Forró1, J. Sokolov1 and M. Rafaîlovitch1; 1Materials Science, SUNY Stony Brook, New York; 2Laboratoire National des Champs Magnétiques Pulsés, Toulouse, France; 3Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

Monolayers (dense arrays) of functionalized multiwall carbon nanotubes (MWCNT) were assembled using the Langmuir-Blodgett (LB) technique in contrast to the standard morphologies of the samples of arrays of nanotubes involving definitions of bundling (ropes, mats, networks, etc.) that are controlled from organic solvent dispersions of pristine nanotubes. The method we propose offers a radical departure from the existing methodology due to the possibility to cover large surfaces with dense thin films of
carbon nanotubes. To our knowledge, up to now, there is no experimental data on electrical and magneto-transport properties of carbon nanotubes or of derivatized carbon nanotubes. We demonstrate that a simple approach of immobilizing carboxylated nile-red fluorescent nanospheres by displacing Br that decorates alloy groups in the irradiated CNT segments. We show that high-spatial resolution site-selective attachment of bioconjugates on ordered arrays of CNTs opens up new possibilities of creating CNT hybrid chips that could serve as combinatorial laboratories for detecting and separating analytes.

2:45 PM GG5.5

**Electrically-Addressable Biological Functionalization of Carbon Nanotubes and Nanofibers**, Chang-Soo Lee1, Sarah E. Babbar1, Matthew S. Madsen1, Mark A. Voigt1, Ernesto Joselevich1,2, A. Ismach1,2,3, L. Segev1, E. Wachtel1, E. Joselevich1,2

One of the major challenges of nanotechnology is the fabrication of high-density biosensor arrays comprised of nanotubes or nanofibers, each modified with distinct biomolecular recognition elements. We have developed a method for electrically-addressable biomolecular functionalization of nanotube and nanofiber electrodes. Using DNA as a prototype, we show that an electrochemical reaction provides a pathway for addressable modification. We verify this by making a small array of distinct DNA oligonucleotides on nanotube electrodes, and show that the resulting DNA-modified nanotubes/nanofibers exhibit excellent selectivity for binding to complementary vs. non-complementary DNA sequences. Furthermore, we demonstrate that the functionalization can be achieved on individual nanotubes and sub-micron fiber bundles without the use of microfluidics. This work provides a practical, inexpensive route toward ultra-high-density, electrically-configurable biosensor arrays.

3:30 PM GG5.6

**Spatial Organization of ZnO Nano-Rods on Silver Surfaces**, Jin W.-P. Hsu, Z. R. Tian, N. C. Simmons, C. M. Matzke, M. A. Rodriguez, J. A. Voigt, Sarah E. Babbar, Sarah E. Babbar, Matthew S. Madsen, Mark A. Voigt, Ernesto Joselevich1,2, A. Ismach1,2,3, L. Segev1, E. Wachtel1, E. Joselevich1,2

ZnO is a technologically important material because of its multi-functionalities that range from piezoelectric transducers and varistors to wide-bandgap semiconductor for UV emitters and detectors. In addition to polycrystalline ceramic powders and epitaxial thin films, recent advances in ZnO have been in vapor-liquid-solid growth of nanowires and solution growth of nanorods. For these nanostructures to be useful, a means to place them strategically on the surface is needed. Here we apply micro-contact printing to selectively modify the growth surfaces with patterned self-assembled monolayers (SAMs), which in turn determines the final spatial organization of ZnO nano-rods.

In addition to spatial selectivity, crystal morphology and hierarchical structures can be tuned through solution chemistry and growth conditions. ZnO nano-rods (grown on Ag film substrates) displayed strong c-axis out-of-plane texture when surrounding regions are covered with mercaptoalkanoic acids (HSC n H 2n COOH). We have achieved excellent selectivity with virtually no nano-rods grown on the SAM regions. The mechanism of selectivity will be discussed. The density of nano-rods inside the patterned Ag areas is substantially higher than that of nano-rods grown on unpatterned Ag. Furthermore, we can control the average density with pattern orders 2 orders of magnitude! In addition, by tuning the feature size and solution chemistry, we are making progress towards growing isolated individual nano-rods on lattices. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
4:00 PM **GG5.8**

**Nano-Carpet Rugs: The Wetting of Vertically Aligned Si Nanorod Arrays**, Yipeng Zhao and Jianguo Fan; Physics and Astronomy, University of Georgia, Athens, Georgia.

The wettabilit"y of a solid state surface is affected by both the surface roughness and the solid chemical composition. Researchers have shown that nanoscale structures such as polymer fiber arrays [1, 2] and carbon nanotube arrays [3], treated by proper chemicals, will produce the super-hydrophobic property. However, a systematic study on the surface of vertically aligned Si nanorod arrays on the properties due to the limitations of the fabrication techniques. Here, we report a systematic investigation on the wettabilit"y of vertically aligned Si nanorod arrays with different heights (aspect ratio) fabricated by the glancing angle deposition technique. The equilibrium water contact angles of vertical aligned nanorod Si films were measured by the sessile drop method. For as-deposited hydrophobic films, there was a contact angle transition from partial composite to composite due to the presence of surfactants (primary amines, phosphine oxides, alkyl phosphonic acids, etc.) which can selectively bind to either the lead precursor or the PbSe wire surface. Depending on the growth rates along (100) and (111) crystallographic directions, we observe formation of either long (up to 30 microns) straight wires with diameter adjustable from 10 to 20 nm or branched stars-shaped nanowires. The use of various stabilizing agents allows us to control the growth of PbSe nanowires as well as PbSe nanorods. By simultaneous control over lateral and longitudinal growth rates, we are able to grow tapered nanowires whose bandgap changes along their length due to the effect of quantum confinement. We propose the technique of aligning PbSe nanowires on-chip by applying an external electric field, thus facilitating their integration into devices. Preliminary electronic measurements demonstrate the potential of solution phase grown PbSe nanowires in FETs and IR active opto-electronic nanodevices.

4:45 PM **GG5.11**

**Assembly of Silicon Nanoparticles Roll Up into Flexible Nanotubes**, Muneer H. Najeef1, Sahraou Chreibi2 and Adam Douglas Smith1; 1Physics, University of Illinois, Urbana, Illinois; 2Theoretical and Applied Mechanics, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We report on flexible nanotubes made of a self-assembly of silicon nanoparticle. We showed that when a colloidal dispersion of fluorescent silicon nanoparticles in alcohol is submitted to an electric field, a current is generated and the particles are driven to one of the electrodes via electrophoresis. This method allows us to coat various surfaces with a thin film of silicon particles. Upon drying, the film rolls up into uniform tubes. Using Atomic Force Microscopy (AFM) and a linear elasticity model we were able to measure the Young’s modulus of this film. It was found to be as flexible as rubber. These structures constitute the basis for enhanced biological recognition and sensing of toxins. Moreover, they are useful as catalysts, and in nano robotic applications.

**SESSION GG6: Poster Session: Mesoscale Architectures**

**Chairs:** Paul Braun, G. Ramanath and Mauricio Terrones

**Terrones**

**Tuesday, Evening, November 30, 2004**

**8:00 PM**

**Exhibition Hall D** (Hynes)

**GG6.1**


We have recently demonstrated a simple and convenient method for
creating active devices from nanometer sized components requires the precise placement of materials in all three dimensions. Colloidal grown quantum dots are typically deposited from solution, using techniques such as spincoating and dropcasting. These solution based processes limit the types of substrates on which deposition can be performed, and also typically require uniformity across the wafer plane and only one at a time. These shortcomings have to date been the primary barrier to the creation of high performance devices utilizing such nanomaterials. By extending the methods of microcontact printing and molding to nanoscale dipolar colloids, we have overcome these obstacles. We demonstrate two dimensional patterned deposition of quantum dots onto diverse substrates, such as silicon, metals, and amorphous organics. This deposition technique has been utilized for the fabrication of bright, highly efficient, and color saturated quantum dot light emitting devices.

GG6.3 Novel Technique for Preparation of Dipolar Microparticles by Polymerization of Polared Emulsions. Vsev. N. Panov1, Olivier J. Cayre1, Hartmut A. Wege1 and Orlin D. Vele2.
1Department of Chemistry, University of Hull, Hull, United Kingdom; 2Dept. of Chemical Engineering, North Carolina State University, Raleigh, North Carolina.

We have developed a novel method for fabrication of dipolar colloidal particles, which is based on polymerisation of oil-in-water emulsions stabilised with a mixture of water-insoluble cationic and anionic surfactants. An emulsion of polymerisable oil in water is polarized in order to 'freeze' the dipolar surface charge distribution. These shortcomings have to date been the primary barrier to the creation of high performance devices utilizing such nanomaterials. By extending the methods of microcontact printing and molding to nanoscale dipolar colloids, we have overcome these obstacles. We demonstrate two dimensional patterned deposition of quantum dots onto diverse substrates, such as silicon, metals, and amorphous organics. This deposition technique has been utilized for the fabrication of bright, highly efficient, and color saturated quantum dot light emitting devices.

GG6.4 Anisotropically Etched Silicon Masters for Nanofabrication. Albert M. Hung1 and Samuel I. Stupp1,2,3.
1Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2Chemistry, Northwestern University, Evanston, Illinois; 3Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

The simple, functional patterning of self-assembling nanostructures on surfaces is a problem of interest in our laboratory. For this purpose we have demonstrated the feasibility of using anisotropically etched silicon as a master mold for generating sub-micron features by a variety of lithographic techniques. The approach involves the use of conventional photolithography and subsequent wet etching of {110} silicon KOH solution to produce a faceted surface structure with [110] ridges as thin as 20nm at the apex. This rigid mold was used to emboss features down to 100nm in a polymethylmethacrylate (PMMA) thin film by nanosprint lithography. Replicas of the mold in polydithiolsiloxane (PDMS) or polyurethane allowed for better conformal contact with the substrate, and a voltage applied between a gold-coated stamp and a silanized silicon substrate resulted in electrically assisted chemical patterning of the silane layer with sub-10nm resolution. This technique could be used for microcontact printing of self-assembled monolayers or patterned electrochemical deposition. This bench-top method could be attractive as a highly versatile way of fabricating complex nanopatterns over a large area without the need for an expensive master.

GG6.6 Nano-patterning of Multiple Self-assembled Monolayers for BioMEMS. Jang Gil Kim, Vincent Blech, Nobuyuki Takama and Beomjoon Kim; Institute of Industrial Science, University of Tokyo, Tokyo, Japan.

Nowadays, with increased demands for nano scale patterning technique, micro contact printing (μCP) has gained much interest as master & replication techniques for its great versatility, high throughput and potentially low cost [1]. However, despite these advantages, difficulties remain in μCP for nano scale patterning. The fabrication of nano scale master of the stamp requires expensive and complicated processes such as EL-lithography. In addition, Sylgard 184 (Shore A hardness, 50), the most commonly used material for fabricating the stamp, enables conformal contact with the substrate due to low hardness, but it is easily deformed and, therefore, leads to collapse effects. Alternative solutions such as composite stamp have been proposed in order to overcome this problem [2, 3]. To make more precise pattern on nano scale with low cost, we studied two methods: the use of micrometer scale pyramidal structure, and a novel hard PDMS stamp. The PDMS stamp was fabricated by solidification of a silica sol, and the substrate was used to obtain pyramidal (or V-shaped) grooves, with
typical width of 4 µm. From such master, a PDMS stamp with sharp tip pyramidal relief was molded, allowing the replication of nano-scale dot patterns of SAM (hexadecanethiol) on CP. However, the deformation and collapse of the stamp still remains as a concern. In order to reduce this effect and, therefore, take advantage of the pyramidal shaped stamp, not only the force on the stamp can be controlled, but its hardness of the stamp was used as well. We used two types of hard PDMS (Shore A hardness, 70) which allowed reaching 500 nm dot patterns with very simple and inexpensive process. Stamps with pyramidal tips or V-shaped grooves then allow reaching the nanoscale, whereas the use of the right combination of stamp and master is necessary. Two stamps of this kind have been used in a second process, consisting in patterning these three different types of molecules self-assembled on the surface of the same substrate. This allows local, selective attachment of biomolecules and other applications. References [1] [2] F. Michel et al., IBM J. Res. & Dev. Vol. 45 No. 5 Sep 2001 and references therein... [2] H. Schmid, B. Michel, Macromolecules 33, pp. 3042-9 (2000) [6] T. W. Odom, J. C. Love, D. B. Wolfe, K. E. Paul, and G. M. Whitesides, Langmuir 18, pp. 5314-20 (2002).

**GG6.7**

Focused Ion Beam Patterning of Transparent Oxide Substrates for Epitaxial Assembly of Colloidal Crystals, Summer K. Rhodes1, Jennifer A. Lewis1,2,3, Paul V. Braun1,3,4 and Ryan J. Kershner1,4,1. Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois, 1Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, Illinois; 2Micro and Nanotechnology Lab, University of Illinois Urbana-Champaign, Urbana, Illinois; 3Beckman Institute for Advanced Science and Technology, University of Illinois Urbana-Champaign, Urbana, Illinois.

Direct writing with a focused ion beam (FIB) was used to generate 2-D square arrays of dimpled features in transparent oxide substrates. These periodic patterns were created with well-controlled hole diameter and depth at a pitch of 500 nm (colloid diameter) to guide the epitaxial assembly of colloidal crystals. In the absence of precise FIB calibration, large variations between the targeted and actual pitch (500 ± 100 nm) were observed for patterns generated. This degree of control is not suitable for colloid templating, since size variations of less than 5% of the colloid diameter are required for crystallization. Through an iterative FIB calibration involving the use of an iterative FIB calibration, the pattern replication error was reduced by an order of magnitude, such that a substrate pitch of 500 ± 10 nm was observed. The effects of ion beam current, beam dwell time, and total milling time on the resulting patterned features were systematically studied. Atomic force microscopy (AFM) was carried out on as-patterned and etched substrates to quantify their uniformity and characteristic feature sizes. By etching, we can generate smooth, enlarged dimpled features free of remnant debris produced during the milling process. Experiments are now underway to explore the epitaxial assembly of colloidal microspheres through gravity-driven sedimentation on these patterned substrates.

**GG6.8**

Site-selective integration of monolayer-protected metal nanoparticles on two-dimensional organic surface templates. Kenseki Asakura1, Jun Hasegawa1, Hidenori Nawaun1, Nagahiro Suzuki2, Osamu Kawanami2,1, Konan University, Kobe, Japan; 2Nagoya University, Nagoya, Japan.

Composite micro- and nano-structures consisting of metal nanoparticles and organic surroundings have recently attracted much attention for both fundamental and practical reasons. In particular, much effort has been devoted to directing monolayer-protected metal nanoparticles into organized structures onto solid supports by a variety of fabrication techniques. One of the emerging techniques for immobilization is to use organic monolayers attached on the nanoparticles and substrate of interest to guide the assembly of the nanoparticles through predesigned chemical and physical interactions. In this study, we demonstrate a novel technique for the fabrication of two-dimensional microscopic assembly of monolayer-protected gold nanoparticles onto substrates. The surface properties of carbonyl acid groups attached on gold nanoparticles were used to guide the site-selective deposition of the nanoparticles onto organic monolayer templates prefabricated on glass substrates. In this approach the gold nanoparticle assemblies were deposited and integrated as two-dimensional microcircuit patterns through the process of simple coating of the solution containing gold nanoparticles and drying followed by solvent-induced lift off. Selective integration of the nanoparticles onto either hydrophobic or hydrophilic region on the substrates could be controlled by changing pH of the solution and by selection of the solvents used for lift-off process, thereby providing effective methodology for fabrication of both positive and negative patterns of integrated mesoscale nanoparticle assemblies.

**GG6.9**

Monolayer and Pattern Formation using Colloidal Particles through Self Assembling Multilayers. Muhammad A. Shetty and Ravishankar Narayanan; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Self Assembled monolayer of colloidal particles find applications in diverse fields such as photonic band gap crystals, physical lithographic mask and diffractive elements for optical sensors. In the present work, monolayers of latex spheres of different sizes ranging from 50 nm -1.6 µm on different plain and micro-patterned substrates have been prepared. Issues relating to the effect of surface charge, concentration of colloidal dispersion, physical nature of the substrate (hydrophilic/ hydrophobic) and anisotropy of the substrate on monolayer/pattern formation are discussed in detail. This leads to useful insight into the process of self assembly and is helpful to control such colloidal layers and crystals.

**GG6.10**

Preferential patterning of metal oxides on metal oxide-recognizing peptides. Site-selective patterning of zinc oxide and europium oxide particles. Mitros Umetani1, Masanouchi Mizuta1, Satoshi Ohara1, Seiichi Takami1, Hideki Tanihara2, Kosuke Tsunomoto2, Izumi Kumaga1 and Tadafumi Adschiri1; 1Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; 2Biomolecular Engineering, Tohoku University, Sendai, Japan.

Recent advances in nanotechnology have enabled us to utilize responses of nanocluster to electron, magnetic and photo fields. The application of nanocluster to electron/photo/electron devices has been attempted, but a new patterning technique apt for nano particle is required. Zinc oxide (ZnO) is one of the most widely used semiconducting oxides for electronic, magnetic and optical applications, so that the patterning of ZnO has been attracting a focus of considerable attention. In this study, we select a peptide with the affinity for ZnO from a phage-display library, and assemble fluorescent ZnO particles on gold plane with the ZnO-recognizing peptide. The phage library with a 12-mer peptide on the surface (Ph.D.-12 Phage Display Peptide Library Kit, New England Biolabs) was applied for selection of a peptide sequence with the affinity for ZnO. The three-time panning procedures resulted in the observation that 24 of 48 phages had the identical displayed peptide sequence. The selected peptide was organically synthesized with a cysteine residue at the C-terminus, and then it was immobilized on an Au film through an Au-S linkage. The peptide-immobilized Au film was soaked in a fluorescent ZnO suspension and washed several times by a detergent solution for excluding nonspecifically-binding ZnO particles. In comparison to an Au film without the ZnO-recognizing peptides, the peptide-immobilized Au film showed an intense fluorescence derived from ZnO. It should be noted that the ZnO-recognizing peptide showed no specificity for europium oxide and zinc sulfide particles. We would show the peptides with the affinity for europium oxide and other metal oxides.

**GG6.11**

A Mesoscale Template Prepared by the Self Assembly of Synthetic Polypeptide. Honggang Cul1, Jeffery Thompson2, Timothy J. Deming1 and Darrin J. Puchan1; 1Department of Materials Science and Engineering, Delaware Biotechnology Institute, University of Delaware, Newark, Delaware; 2Department of Materials and Chemistry, University of California at Santa Barbara, Santa Barbara, California.

Control of the detailed structure of matter on many length scales is a major goal of chemistry, materials science and nanotechnology. The structure and function of synthetic polypeptide single crystal surfaces may provide a useful base to template material growth from the nanoscale to macroscale level. Single crystals of synthetic poly(1-lysine) (PLL) polypeptides have been grown up to many microns in diameter from aqueous solution by the addition of salts or nonsolvents. Circular dichroism (CD) data showed that the crystal structure was defined on the nanoscale by the alpha helical secondary structure of PLL chains in the mother solution, which can be controlled by either pH or temperature. The resultant single crystals morphologies were studied by transmission electron microscopy (TEM), atomic force microscopy (AFM), and field emission scanning electron microscopy (FESEM). PLL single crystals exhibited the forms of regular hexagonal lamellae in both monolayer and multilayer forms with or without a central screw dislocation depending on the growing conditions. The thickness of the resultant crystals can be directly controlled by the PLL molecular weight. The local hexagonal lattice structures of single crystals both in solution and in film were obtained by X-ray scattering and electron diffraction. The application of polypeptide single crystals as templates to control the crystalization of minerals and the assembly of metal nanoparticles was initially investigated.
GG6.12 Fabrication of Highly Ordered Anodic Porous Alumina using a Self-Organized Particle Array. Yoshinori Matsumoto1, Futoshi Matsumoto2, Kazuyuki Nishio1,2, and Hideo Masuhira2.1; 1Kanagawa Academy of Science and Technology, Kanagawa, Japan; 2Tokyo Metropolitan University, Tokyo, Japan.

Highly ordered anodic porous alumina, which has a fine channel structure with uniform-sized holes of nanometer scale and high aspect ratios, has recently attracted much interest as a starting material for the fabrication of a variety of nanomachined structures of kinds of nanodevices. We have reported that an ideally ordered single domain hole array structure with uniform straight channels and ideal hexagonal arrangement could be obtained by adding anodization of Al to the pretexturing process of Al with a master for generating the array of concaves on the surface of the Al substrate.1 The array of concaves initiates the development of pores. 2 However, the master used was a SiC mold prepared using expensive electron-beam lithography and ion-etching apparatuses. In the present work, we show a new preparation of anodic porous alumina with highly ordered submicron-sized channels by means of a polystyrene particle array formed by self-organization of the particles as a master.1 Two-dimensional ordered array of polystyrene particles with 200 nm in diameter was fabricated on the glass plate by slowly evaporating the water solvent in which polystyrene particles were dispersed. An Al layer was deposited on the two-dimensional ordered particle array by vapor deposition. The polystyrene particles were removed from the deposited Al by immersing the Al substrate into toluene. Anodization of the Al substrate was carried out at a constant voltage. The fabrication of an ideally arranged hexagonal cell configuration having a cell size of 290 nm which corresponds to that of the pretextured concaves on the surface of deposited Al was confirmed. This result demonstrates the feasibility of employing self-organized particle array as a master for the fabrication of long-range-ordered channel array architecture. [1] H. Masuda et al., Appl. Phys. Lett., 71, 2770 (1997). [2] H. Masuda et al., Chem. Lett., 33, 584 (2004).

GG6.13 Self-Assembled Mesoscale Hollow Capsule Reactor for Unusual Material Synthesis. Won San Choi, Jeong-Ho Park, Hyo Young Koh, Seung Hwan Oh and Dong-Yu Kim; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Recently, a new concept of chemical synthesis of organic/inorganic materials inside or surface of polyelectrolyte hollow capsules was introduced. However, most of these include the synthesis of nanosized magnetite or organic materials. As far as polymerization reaction is concerned, there are only a limited number of reports. We have investigated the difference of polymerization reaction between inside and outside of hollow capsules having confined geometry. A water soluble initiator bound hollow capsules were used as a nanoreactor. After polymerization, the shape of capsules could be manipulated by monomer concentration changes. The polymers grown from inside as well as the polymers grown from outside. This polymerization behavior could be further controlled by the capsule size and monomer contents.

GG6.14 Colloidal Clusters of Silicon or Polymer Microspheres. Gu-Ha Lee1,2,3, Minsung Song1,2,3, Yunn Jeong Yang2, David J. Pine2 and Seung-Kun Lee3; 1 Corporate R&D Center, LG Chem Co., Daejeon, South Korea; 2Department of Chemical Engineering, University of California, Santa Barbara, California; 3Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon, South Korea.

We demonstrate an emulsion encapsulation and shrinkage technique for producing large quantities of colloidal stable clusters of highly monodisperse microspheres, including sterically stabilized silica, poly(methyl methacrylate), and polystyrene particles. We find that the sequence of cluster structures is identical for the three systems when the nonane water to toluene ratio is less than 1. Despite the differences in particle properties and interactions in the fluid systems, the sequence of structures remains remarkably consistent even at larger n, suggesting that the sphere packing process may work for a wide range of colloidal materials. The gelation and robust process can be used to prepare clusters with shapes such as dodecahedra, icosahedra, and others, all of which can be rendered colloidal stable in either oil or water through a simple silica coating technique.


Information of a protein’s structure is essential for the understanding of its function. Protein crystallization to obtain crystals large enough for X-ray diffraction is often the bottleneck in the structure determination process. We investigate two routes to by-pass this problem: the use of electron diffraction since electron diffraction requires much smaller crystals (typically 100 times smaller) and the use of tailor-made substrates to enhance the initial crystallization. Concerning the latter, we have applied nanotechnology (“bottom-up” in contrast to “top-down” processes) combined with self-assembly of protein molecules. As “bottom-up” processes, optical, electron beam, and focused ion beam lithography methods are used to make nano-patterned a-SN (amorphous-Silicon Nitride) substrates. These a-SN membranes are used for a substrate to put on protein molecules by “bottom-up” process as like a self-assembly process. We will discuss the preparation and characterization of the tailor-made substrates and their effectiveness in the assembly of protein molecules.

GG6.16 Nanostructured Nanoparticles: A Novel Material to Prevent Protein Non-Specific Adsorption. Alvin M. Jackson and Francesco Stellacci; Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Recently, we have developed a new class of nanomaterials.1 These are monolayer protected metal nanoparticles coated with a mixture of ligands that spontaneously forms sub-nanometer phase separated domains. In the case of two ligands, in which one is hydrophobic and the other is hydrophilic, ring of alternating composition form and create the nanoparticle core. The hydrophobic or hydrophilic region is no more the 6 A wide. Proteins are known to nonspecifically adsorb on surfaces by a mechanism that involves conformational change and maximization of the attractive electrostatic forces. van der Waals and electrostatic forces between the material surface and the protein’s exterior. This type of mechanism is inhibited in the case of protein adsorption on surfaces evenly coated with hydrophobic/hydrophilic nanostructured nanoparticles. In fact, each domain on the particle’s shell is as small as a single amino-acid, thus the protein is not solely attracted or repelled to such surfaces. As a consequence the net interaction force between the protein and the surface is smaller then the solvation energy and proteins tend to stay in solution. Here we will present a series of measurements that aims at the systematic understanding of the intra-molecular interactions between proteins and nanostructured nanoparticles. In particular, quantitative comparisons (made using FTIR, XPS and fluorescence microscopy) between the protein resistance of surfaces coated with these particles and surfaces coated with industrial standards, such as polycrylenyl-glycols, will be presented. High Resolution Force Microscopy (HRFS) results coupled with theoretical models have been used to elucidate the protein structure and the molecular nature of the interactions between the ligand shell nanodomains and the proteins. The main results will be presented. Also, preliminary results in decoupling the solvation effects from the intra-molecular effects will be discussed. 1 A. Jackson, J. Myerson, and F. Stellacci, Nature Materials 2004, 330.

GG6.17 Two-Dimensional DNA-directed Assembly of Colloids into Defined Arrays. Margaret H.S. Shyr1,2, Robert A. Barry1,2, Pierre Wiltzius1,2 and Paul V. Braun1,2; 1 Materials Science & Eng., University of Illinois Urbana-Champaign, Urbana, Illinois; 2Beckman Institute, Urbana, Illinois.

DNA-derivatized polystyrene nanoparticles were assembled onto DNA-functionalized surfaces in spatially-defined two-dimensional domains by exploiting highly specific Watson-Crick binding interactions that occur between complementary single-stranded DNA. Using microcontact printing, a glass substrate was patterned with ssDNA. Polystyrene colloids were functionalized with complementary ssDNA. Via hybridization of the ssDNA nucleotides, we were able to direct the colloid assembly onto the substrate into a variety of patterns, including periodic structures, which were studied through simple laser diffraction. Fluorescence microscopy confirmed that assembly did indeed occur through specific DNA hybridization and not through nonspecific interactions: colloidal particles functionalized with non-complementary ssDNA did not bind to the surface. High resolution imaging of the two-dimensional assembly pattern was done using SEM. Finally, in DNA assemblies are temperature sensitive, we have investigated the response of the colloidal assemblies to thermal annealing.

Physico-chemical effects such as pH, ionic strength, and temperature, on self-assembly have been studied. An attractive approach to repetitive polypeptides for application to nanoscale building blocks, templates, and device construction were studied by various methods including surface probe microscopy and novel deep UV Raman spectroscopy. The different factors that modulate the folding of repetitive polypeptides to the secondary, tertiary, and quaternary structures, and the monomers to the mesoscopic fibrils by intermolecular assembly are discussed. The repetitive and block-copolymerized β-sheet forming polypeptides have been prepared by a general strategy for libraries of artificial repetitive DNA sequences that were prepared based on unidirectional head-to-tail polymerization. The DNA oligomerization/block copolymerization was performed in the presence of a phosphoethanolamine residue in a type Hs restriction endonuclease for regeneration of assembled DNA units with non-palindromic cohesive ends. Repetitive coding sequences were successively constructed in a reproducible and predictable manner without the need for special cloning vectors while suppressing the intranomolecular cyclization of multimers that is problematic when longer sequences are constructed. Several amphipathic repetitive polypeptides were designed, coded, and constructed. Constructed DNAAs were expressed in standard and commercially available E.coli expression systems. Results for several key peptides are discussed focusing on those structures with customised length and functionality. The physico-chemical properties of these polypeptides are also discussed within the context of a protein-concentration-based method for separation of fibrils and monomers.

**GG6.19 Controllable Growth of Nanowire Arrays in One Dimensional Solid-State Nanoreactors.** Andrei Anatolievich Eliseev1, Kirill Sergeevich Napolitski2, Irina Valerievna Kolesnik3, Alexey Viktorovich Lukashin1, Yuri Dmitrievich Tretyakov4 and Peter Goernert2; 1Department of Materials Science, Moscow State University, Moscow, Russian Federation; 2INOVENT e.V., Jena, Germany.

One of the most challenging tasks in materials science today is the preparation of nanomaterials with the controlled properties and dimensions as well as creation of functional nanomaterials. The most challenging nanosystems are one-dimensional particles or nanowires owing to highest anisotropy parameters in them, which could certainly increase functional properties of nanomaterials. However, the use of the nanomaterials is strongly restricted because of their low stability. The approach to this problem is the preparation of the so-called nanocomposite materials. This enables one to avoid aggregation of nanoparticles and protect them from external influences, which simplifies application of such materials. Thus, the main goal of this work is considered as elaboration of basic principles for preparation of nanoparticles with controlled physical properties in one-dimensional solid state nanoreactors (such as mesoporous silica, mesoporous aluminosilicates, alodic aluminas, etc.). The study represents the formation of magnetic, semiconductor and catalytic nanocomposites based on the metallic (Fe, Ni, Ag, Pt, Pd, Cu–Co, Fe–Pt alloys, etc) and metal oxide (α-Fe2O3, γ–Fe2O3, Fe3O4, etc.) nanowires grown in one-dimensional solid-state nanoreactors. Nanocomposites were characterized by chemical analysis, HRTEM, ED, SEM, SAXS, SANS and magnetic measurements and optical spectroscopy. It was shown that particles shape and size are in good agreement with the shape and size of the pores in 1D nanoreactors, while the average length of nanowires could be varied in a wide range. Particles are uniform and well ordered in the matrices. Thus, our approach leads to functional materials with nanosized active elements in the matrices, which could find an application in various fields of engineering and technology. This work is supported by RFBR (03-03-32182) and INTAS (01-204).

**GG6.20 Nanotube characterization through radial distribution function measurements using neutron diffraction.** Pedro Armando Ojeda1, Darin Hoffman2, Mauricio Terrones1, Humberto Terrones2, Thomas Proffen2 and Anthony Cechetto2; 1Materials Advanced, Instituto Potosino de Investigacion Científica y Tecnológica, San Luis Potosi, Mexico; 2Physics, Boston College, Chestnut Hill, Massachusetts.

The reduced radial distribution function G(r) of different types of nanotubes (different diameters and chiralities) has been calculated. We find that the G(r) could be used to distinguish arm-chair, zig-zag and chiral nanotubes. Trigonal arrangements of arm-chair nanotubes with different diameters possess characteristic features. In the case of zig-zag nanotubes, the G(r) signals also exhibit typical patterns that make them recognizable. Experimental G(r)/s, obtained from neutron scattering of single walled carbon nanotube samples, are in agreement with the calculated G(r)/s of arm-chair nanotubes with diameters ranging from 10 Angs. to 14 Angs. Certainly, chiralities around these arm-chair cases cannot be excluded. The analysis of the zig-zag nanotube bundles is also discussed.

**GG6.21 Selective Growth, Diameter Control, and Mechanistic Study of Copper Oxide Nanowires Grown from Exposed Edge of Al2O3/Cu/Al2O3 Thin Film Multilayer Structure.** Nitin Chopra1, Bruce Jackson Hinds1, Chemical and Materials Engineering, Univ. of Kentucky, Lexington, Kentucky.

High aspect ratio and rigid structure of oxide nanowires (NWs) make them useful for nanoscale circuits, interconnects, NEMS, and sensing. For such applications selective growth and diameter control of NWs is crucial. There are several examples of CuO NWs grown by methods as simple as heating Cu foils in air. Our research focuses on diameter control of CuO NWs on patterned silicon substrate by using the dimensional control of narrow lines of Cu (40-100nm) formed at the cleaved/etched face of a A1203/Cu/Al203 multilayer structure. Such thin film patterning eliminates the necessity for e-beam lithography as the film thickness determines nm-scale line dimension. The NWs were characterized by SEM, TEM, and EDS studies. NWs were observed to grow only from the ‘mesa’ structure with average diameter of 39, 47, and 88 nm were observed for Cu line width of 40, 60 and 100 nm respectively when heated in air at 400°C for 60 min. The standard deviations were 6.7, 8.5, and 26.3 nm indicating larger line widths allow larger deviation in nucleation sites. The NWs grow with tilt diameter smaller than base diameter with an aspect ratio as high as 9, 12 for Cu line width of 40, 60, 100nm respectively. The TEM study revealed that NWs were grown against a thick Cu film (on a Si3N4 membrane TEM window as a substrate) at 400°C showed presence of defects/dislocations at the base of NWs indicative of role of metal defects in nanowire growth. The minimal thickness of Cu film for NW growth is about 150 nm at growth temperatures of 500°C and 600°C. This minimum thickness is reduced to 40 nm at 400°C. EDS study shows NW composition as CuOx (x = 1.2-1.4). CuO NWs grown at 400°C have diameters that are determined by Cu line width in multilayer thin film structures. This can be the basis for the directed growth of multidimensional mesostructures of CuO NWs based common thin film fabrication technology.

**GG6.22 Electrochemical Fabrication of Mesostructured Metal Nanotubes from Lyotropic Liquid Crystaline Phases.** Hoangvi Luu, Donghui Wang and Yungfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

The discovery of carbon nanotubes in 1991 has initiated intense interest in synthesizing different kinds of tubular structure materials. For example, the metal nanotubes can be prepared by templating synthesis, such as electrochemical deposition of metal in the pores of the template membranes either by using pulse voltage electrodeposition for short time results in nanotube with only 2µm length, or by using anodic etching as the as the one-stage electrodeposition to modify the pore-wall of the template. Lyotropic liquid crystalline phases formed at high concentrations of non-ionic polyoxyethylene surfactants can be utilized as versatile nanoscale molds for the formation of highly ordered hexagonal mesoporous metal or semiconductor films. In this work, we extend this technique to electrodeposit crystalline nickel and cobalt nanotubes in porous anodic alumina oxide (AAO) membranes from lanmilatry liquid crystalline phases. The liquid crystalline templates are characterized by low-angle X-ray diffraction (XRD) and polarized-light optical microscopy (POM). The nanotubes are characterized by wide-angle XRD, field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). The obtained mesoscopic crystalline nanotubes exhibit ordered mesoscale lamellar structure. The length of nanotubes is easily controlled from several hundred nanometers to tens micrometers by electrodeposition time and the maximum length is the thickness of the template membrane. The magnetic properties of 200 nm sized nickel tubes exhibit anisotropy and coercivity of about 100-120 Oe, comparable to nanowires, higher than nickel film.

**GG6.23 Fabrication of Triangular Lattice Arrays of Nano-Dots and Aligned Carbon Nanotubes.** Yang Wang, J. Rybczynski, Dezhi Geer1, Igor K. Lechn1 and John T. Welch; 'Department of Materials Research Laboratory, Unv. of Kentucky, Lexington, Kentucky.

A two-step masking approach has been invented utilizing self-assembly of polystyrene nanospheres to prepare triangular lattice arrays of nanodots at low cost. A mask of self-assembled nanospheres were used as the first mask to construct a secondary mask by
sputtering Ni onto the spheres. This secondary mask was immediately 
used to pattern triangular lattice arrays of nano-dots. Aligned carbon 
nanotubes with triangular lattice pattern were grown for the first time 
from the periodic Ni dots so prepared. Another two-step technique 
was also invented soon after to successfully obtain triangular lattice 
arrays of nano-dots as well as aligned carbon nanotubes in a very 
large scale. This method is also applicable to a variety of nano-dot 
materials on any flat substrates for different application purposes. 

**GG6.24**

Large-Scale Periodic Nanotubes and Nanowires Arrays - 
Their Fabrication, Modifications, and Properties.

Jakub Rybczynski, Yang Wang, Debasish Banerjee, Dezhi Wang, 
Krzysztof Kempa and Zhiheng Ren; Physics Dept., Boston College, 
Chostnt Hill, Massachusetts.

Self-assembly process of polymer microspheres has been proven as a 
very simple and cost-effective technique for preparation of large-scale 
arrays. These arrays can be used for growth of carbon nano-
nanotubes or nanowires with controlled periodicity. The separation of 
individual nanotubes nanowires and their arrangement can be 
modified by the use of different diameter microspheres, mask heating, 
a double-anodized aluminum wire. Due to their long-range periodicity 
these latexes may exhibit interesting optical properties such as photosonic bandgap behavior, antenna effect, or laser action. Recent results of nanotubes and 
nanowires arrays preparation, nanowires and carbon nanotubes, and their optical properties investigations will be presented.

**GG6.25**

 Branched and Hyper-branched Nanowire Structures as 
Building Blocks for Nanoelectronics and Nanophotonics.

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Bradley and hyper-branched silicon nanowire structures were produced 
via a multi-step nanocluster-mediated synthesis using 
chemical vapor deposition. Scanning electron microscopy studies 
confirmed the formation of branched nanostructures and 
thereby showed that the density of nano-branching can be controlled in a 
predictable manner. This approach was also used to grow 
random gullitide nanotube nanowires. High-resolution transmission 
electron microscopy studies revealed that single-crystal nanowires 
grew epitaxially from backbone, e.g., silicon nanowires with 
growth direction of <111> branched out from silicon nanowires with 
growth axes of <111>. Multiple generations of nanowire branches were 
grown epitaxially from nanowire backbones with well-controlled 
composition/doping, and specifically individual silicon-based 
nanotubes or carbon nanotubes can be used. The ability of sequential 
branching opens up new opportunities for both fundamental studies and nanoscale materials/devices 
application, including three-dimensional nanoelectronics.

**GG6.26**

Anodized Aluminum Templates for Nanowire and Carbon 
Nanotube Field-Effect Transistors.

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2Laboratoire de Physique des Interfaces et des Couches Mince, ECOLE Polytechnique, Palaiseau, France.

Anodized aluminum forms a self-assembled, triangular network of 
nanometer diameter pores that are used as templates for 
nanostructure synthesis. This is because the pore diameter, 
distribution, and length can be tailored to suit the needs of the user 
by varying the anodization conditions: electrolyte, voltage, time, and 
temperature. The chosen pore size determines the resulting 
nanostructure dimensions. Another reason is that once the 
microstructure has been made in the aluminum oxide template they 
can be electrically contacted at the top and bottom of the membrane 
for physical measurements without the need for lithography. With two 
contacts a scientist can study many interesting phenomena such as 
magnetotransport and photoresponse in nanotube transistors. 
One contact, however, is not enough if one wants to make a device such as a 
transistor for applications or research. A third contact or electrode 
is needed. An aspect of our research is the development of templates 
that allow placement of a third electrode close enough to the 
nanowires or carbon nanotubes for an electric field effect. At this time 
we have two possible template structures for field-effect transistors. 
The first structure starts with an aluminum wire which is anodized 
perpendicular to its axis to form an isolation layer onto which a gate 
electrode is sputtered and then anodized again to form a network of 
contacts parallel to the wire as a template for the synthesis of 
nanowires arrays. The nanowires arrays can be grown on the gate 
electrode already in place. Preliminary results have been 
obtained with tellurium nanowires. This structure is interesting for us 
because it can be made totally in our lab without the need for a clean 
room or lithography. This same approach was also used to grow 
ordered arrays of nanowires, embedded in photoresist. The flexibility offered 
by the lithography method enables us to co-fabricate the nanotube 
array with silicon for firms gripping of the specimen, thus 
validating the related theoretical and computational research. For 
obtaining a reasonable estimate of the carbon nanotube properties, it 
is also important to conduct experiments on a single free-standing 

**GG6.27**

Wafer-level Ordered Arrays of Aligned Carbon Nanotubes 
with Controlled Size and Spacing on Silicon.

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3Institute of Materials Research and Engineering, Singapore, Singapore.

Ordered arrays of well-aligned multi-walled carbon nanotubes (CNTs) 
have been fabricated using perfectly-ordered porous alumina 
templates on silicon. Single-domain porous alumina with regular 
periodicity over an entire wafer was achieved by anodizing a 
mixture of aluminum evaporated on nanoscale-corrugated silicon surfaces. The silicon surface was patterned using interference lithography, 
and periodic arrays (with hexagonal and square symmetry) of inverted 
pyramid structures were formed through anisotropic wet etching. 
Anodization of aluminum films deposited on these corrugated surfaces 
led to periodic pore structures with the pore spacing and symmetry 
determined by the pattern etched into the silicon. Nickel was 
evaporated into ordered alumina templates and ion-milling was used 
to remove the excess nickel from the surface of the porous alumina. 
The resulting Ni nanodots at the base of the pores catalyzed CNT 
growth inside the ordered porous alumina templates during plasma 
enhanced chemical vapor deposition with acetylene and ammonia at 
700-750°C. The resulting multi-walled carbon nanotubes were 
characterized using SEM, TEM and Raman spectroscopy. These results 
demonstrate a wafer-scale approach to control the size and 
position of carbon nanotubes and other nanoscale elements (including 
both metallic and semiconductor nanotubes) in a rigid insulating 
scaffold. We will also discuss other wafer-level approaches to obtain 
aligned & ordered carbon nanotubes with sub-lithographic spacing.

**GG6.28**

Lithographically Fabricated Free-Standing Carbon Nanotubes 
Specimens Embedded in Polymer. Amin Desai and Aman Hoehe; 
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We present a novel lithographic technique for fabricating free-standing 
carbon nanotube specimens. Our technique can also be used to 
fabricate free-standing specimens of other nanostructures (nanotubes 
and nanowires) in polymer or metal. Free-standing specimens 
are preferred for experiments to determine mechanical, thermal, electrical 
and electromechanical properties of nanotubes and nanowires and also 
their interaction with other materials and environments like interfacial 
mechanics of composites. The proposed fabrication technique is based 
on the 'photolithography' process, which is widely used in 
nano-fabrication processes to create nanometer size patterns. The 
technique consists of dispersing nanotubes and photoresist (a 
photosensitive polymer) mixture on a substrate and using 
photography to define the placement and density of nanotubes. 
The fabrication process allows us to integrate specimens with MEMS 
based sensors and actuators, which on account of the 
scaling (micro level) have very high resolution. The fabrication 
of nanotubes in polymer provides for firm gripping of the specimen, thus 
enhancing the quality of experimental data. The fabrication technique 
proposed is robust, repeatable and flexible. We have prepared free 
standing specimens of carbon nanotube in photoresist and are 
developing such specimens of carbon nanotubes for mechanical, 
thermal and electromechanical testing. In order to obtain the 
unique length scale dependant properties of carbon nanotubes, it is 
essential to perform experiments to characterize carbon nanotubes to 
validate the related theoretical and computational research. For 
obtaining a reasonable estimate of the carbon nanotube properties, it 
is also important to conduct experiments on a single free-standing
carbon nanotube specimen. Various challenges exist for direct experimental determination of carbon nanotube properties and their interaction with material and environment, like integration with high resolution sensors and actuators and firm gripping of the specimen. Additionally carbon nanotubes embedded in polymer specimen are required to perform various kinds of interferential testing; the information from such arrays can help to elucidate for fabrication of carbon nanotube polymer composites. Carbon nanotube polymer composites are claimed to possess exceptionally good mechanical, thermal and electrical properties. However in order to exploit these properties it is necessary to perform interferential testing to support the claims made by theory. The information obtained from such experiments will not only aid in understanding of interfacial characteristic but will also be useful in manipulation of the interfaces for improved nanocomposites.

**GG6.29 Thermally Controlled Growth of Nanowires, Ton Harris**, Debasis Bauercr, Zhifeng Ren and Gang Chen, Mechanical, MIT, Cambridge, Massachusetts; 3Physics, Boston College, Chestnut Hill, Massachusetts.

Nanowires and nanotubes possess numerous attractive physical properties for potential use in electronics, photonics, sensing, and energy conversion. The synthesis of nanowires has become relatively simple using a variety of fabrication methods now available, such as vapor-liquid-solid (VLS) growth and pressure-injection-implantation techniques. However, despite the relatively simple nanowire synthesis (compared to epitaxial-film growth), nanowire devices are far from mass production. One of the key issues impeding the large-scale development of nanowire devices is that nanowires, as synthesized, are usually oriented in a random manner. Current methods for producing devices out of random nanowire arrangements typically result in one of the few proof-of-principle devices by, for example, randomly dispersing nanowires on a wafer with existing electrodes in hopes of making a few good electrical contacts. Recent attempts to place aligned wires in desired locations rely on microfluidic shear-stress flows coupled with surfactants for wire selective, Nevertheless, because of the low success rate in placing nanowires in desired locations and an equally low yield of viable devices, these post-nanowire growth processing methods are not practical as fabrication techniques for mass-producing devices. A different aligned approach is to control the orientation during the growth process through external electric fields. This method employs a field similar to that used in plasma-enhanced chemical vapor deposition (PECVD) and was first to demonstrate growth of carbon nanotubes and self-assembled nanowires perpendicular to the substrate.

Although this wire-growth method can be advantageous, nanowires grown vertically from the substrate typically are not compatible with conventional microelectronics, which are based on in-plane devices. A few researchers have developed experiments, particularly in carbon nanotube growth, where an electric field is applied in a direction horizontal to the surface to grow nanotubes parallel to that surface. These approaches, however, have not yet succeeded in making wafer-scale devices. A method for controlling the location and directionality of nanowire growth is based on thermally activating a single nanowire catalyst particle in the VLS process to initiate selective wire growth and placement, while employing an electric field to guide the wire to a desired direction. This technique is demonstrated using resistive heating with platinum microheaters. With this simplified approach we observe selective nanowire growth due to the locally heated region of the heater and also observe the effects of an applied electric field on wire growth directionality.

**GG6.30 Highly Oriented Plate-Like Nanorods Arrays of ZnO**, Ying Du, Yao Jin Li, Xin Mei Pei and Long Qiang Zhou, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, China.

Highly oriented plate-like nanorods arrays of ZnO are synthesized by solution-based approach at low temperature. ZnO nanorod arrays grown vertically on the silicon substrate and the nanorod consists of the plate of plate-like ZnO single-crystal along the c-axis direction. The construction of plate-like arrays is achieved by varying the growth conditions. The growth mechanism is analyzed by XRD, SEM, TEM and HRTEM based on the nuclear and growth process of ZnO. Photocatalytic properties of the nanostructures are investigated. Moreover, ZnO nanorod arrays are expected to have great potential for sensing, catalysis and optical emission.


During attempts to fabricate ZnO nanowires, we accidentally observed the growth of SiOx nanowires on Au coated Si substrate. Detailed characterizations on the resulting nanowires were carried out by field-emission scanning electron microscopy, transmission electron microscopy, reflectance infrared spectroscopy, X-ray photoelectron spectroscopy, and X-ray photoelectron spectroscopy. The resulting nanowires have a Si-to-O ratio of 1.16, and a diameter ranging from 50 nm - 300 nm. It was found that the presence of Au substrateplays a key role in the formation of SiOx nanowires. A systematic investigation of how the growth conditions, such as the growth temperature, the oxygen to Ar carrier gas ratio, and the growth time, affect the formation of SiOx nanowires, was performed. A high growth temperature (350 °C) and a high oxygen gas flow (250 SCCM Ar and 5 SCCM O2) helped promoting the growth of long nanowires. The diameters of nanowires increased with the growth time. It was demonstrated that the formation of the SiOx nanowires was due to a solid-state-solid mechanism. In a local catalytic oxidation of CO by Au nanoclusters played a role in accelerating nanowire formation.

**GG6.32 Peptides with Selective Affinity for Carbon Nanotubes**, Caroline Lau, Yet-Ming Chiang and Steve Lustig, Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Dupont Central Research and Development, Experimental Station, Wilmington, Delaware.

The use of biological molecules to facilitate the dispersal, separation and assembly of nanoscopic entities such as carbon nanotubes has received great attention and has been the focus of much current research activity. In this work we sought to identify peptide sequences with selective affinity for HiPco-produced SWNTs (single-walled carbon nanotubes) in order to gain some insight into the binding mechanisms and interactions. This was done using a phage display technique, in which a library of bacteriophages displaying greater than 10^6 different 12-mer peptide sequences were exposed to carbon nanotubes. Non-specifically bound phages were successively washed off with increasingly stronger detergents until only tightly binding phages remained. It was observed that after six rounds of phage display tests, the percentage of sites of aromatic ring-containing amino acids increased while the percentage of sites of aliphatic amino acids decreased. Results were compared to previous phage display results on MWNWs (multi-walled carbon nanotubes). These results suggest that peptides are able to distinguish between different allotropes of carbon and that their highly specific binding mechanisms can be exploited in the future for precision placement of nanoscale components in devices such as electronic circuits and sensors.

**GG6.33 One Directional Alignment of the Metal/Oxide Hybrid Nanotube with Self-Assembled Monolayers (SAMs)**, Daekyu Jeong, Jaeeg Lee, Hyunjung Shin and Jiyoung Kim, Advanced Materials Engineering, Kookmin University, Seoul, South Korea.

Various fabrication methods on oxide and metal nanotubes have been investigated due to their excellent physical and chemical properties. In order to use appropriate the nanotubes, it is important to develop technology to align the nanotubes and integrate into a system. In this paper we demonstrate a novel methodology on aligning metal/oxide hybrid nanotube in one direction can make the metal and oxide nanotube array using self-assembled monolayer(SAM) on Si wafer. We have fabricated metal/oxide hybrid nanotube using conformal and selective deposition techniques atomic layer deposition (ALD) and SAM on nanotemplates. This technique allows to fabricate nanotubes precisely on the control of wall thickness with a few tens nanometers of height and a few micrometers of length on soluble nanotemplates. We used organic base materials (polycarbonate) nanotemplate supplying uniform nano-scale pores. Then we performed surface treatment using SAM on the nanotemplate in order to achieve selective deposition. And we deposited conformal and uniform thin metal oxide tube wall using ALD. Polycarbonate nanotemplate was perfectly removed by vacuum filtering after dissolving in the solvent, such as Chloroform, then metal/oxide nanotubes were wetted with hydrophilic SAMs (Hexadecanethiol:HDT). The metal/oxide nanotubes were coated with HDT. We patterned Si/SiO2 substrates using soft contact printing with OTS (Octadesyl-tetrachlorosilane) inks which transfer Si/SiO2 substrate properties from hydrophilic to hydrophobic property. Hydrophilic property and hydrophobic property are inundated on one direction following Si wafer line, otherwise there is no nanotubes on OTS line pattern. The various properties of the resultant metal oxide nanotube were examined with a number of techniques of HR-TEM, FE-SEM, EDX, and AFM. We also observed metal nanostructure, direction with high resolution sensors and actuators and firm gripping of the specimen.
Compositionally modulated nanowires are attractive building blocks for nanophotonics and nanoelectronics. For example, control of the structure and composition during nanowire synthesis can define their photonic properties, such as emission wavelength or color. Here we report growth and structural investigations of radially-modulated GaN/InGaN/GaN core-shell-shell (CSS) nanowires, whose composition can be provided by one-step chemical reduction in the 0.8-3.5 eV energy range. GaN nanowires were first grown by a nanocluster-mediated growth, and then sequentially overcoated by InGaN and GaN nanoscale shells. All of the growth steps were carried out continuously using metal-organic chemical vapor deposition. Bright-field transmission electron microscopy (TEM) images combined with energy dispersive X-ray spectroscopy (EDX) demonstrate (i) diameter control of the starting GaN nanowires by the size of the catalytic nanoparticles and (ii) epitaxial growth of the shells. These TEM studies further reveal defect-free CSS nanowire structures, which should provide a unique advantage compared to dislocation-rich, GaN-based planar structures. Electron diffraction and high-resolution TEM images show that the CSS nanowires have a wurtzite structure, (11-20) growth direction, and triangular cross-section defined by (0001) and two {1-101} crystallographic planes. These data were used to construct a CSS structural model that successfully fits EDX compositional line profiles, and allows calculation of the core and shell thickness. Taken together, these data demonstrate that GaN/InGaN/GaN CSS nanowires were grown having single crystalline and dislocation-free structure, smooth surface and radially modulated composition. The high yield and compositional control of GaN/InGaN/GaN CSS nanowires achieved in our work provide an essential step towards future nanoscale applications, such as nanoscale light emitting diodes and lasers.
Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Large-dimension colloidal crystals were created by gravitational settling of colloidal microspheres onto patterned substrates. The large-area patterned substrates were produced using multibeam-beam interference lithography facilitating the controlled growth of single-domain crystals with controlled crystallographic orientation. A 2-beam UV laser setup was employed to produce 1-D features with a periodicity on the order of 500 nm (diagonal diameter). This was extended to a square array of 2-D features through multiple exposures or multiple beams. Atomic force microscopy (AFM) was used to characterize the resulting surface features. The exposure parameters were varied to control the depth and width of features in an attempt to optimize the pattern for two-dimensional colloidal epitaxy. Colloidal crystals were produced from a binary suspension of colloidal microspheres stabilized through the addition of highly charged nanoparticles (Tohver et al., PNAS (2001)) followed by subsequent nanoparticle gelation (Lee et al., Langmuir (2004)) to yield robust structures that can withstand capillary forces during drying.

GG6.42
Synthesis and Self-Assembly of Hydrogel Nanoparticles with Interpenetrating Polymer Networks. Xiaohu Xia and Zhibing Hu; Physics University of North Texas, Denton, Texas.

Monodisperse nanoparticles composed of polyelectrolyte (PAAc) and poly(N-isopropylacrylamide) (PNIPAM) interpenetrating polymer networks (IPN) were synthesized by two-step method with first preparing PNIPAM nanoparticles and then polymerizing acrylic acid into the PNIPAM nanoparticles. The growth kinetics of the IPN particle formation was obtained by measuring the turbidity and particles hydrodynamic radius (Rh) as a function of reaction time. Individual IPN and PNIPAM nanoparticles were characterized and compared using dynamic and static light scattering techniques. The concentrated aqueous solutions of the PNIPAM-PAAc-IPN nanoparticles can change from a fluid at room temperature to a physically bonded nanoparticle network above a gelation temperature about 360C. The PNIPAM provides physical bonds between particles via a temperature-dependent interparticle potential, while PAAc in the neutral pH provides ionic charges that are temperature-independent and prevent the collapse of the particles into an aggregate. This system exhibits a rich phase behavior, including a colloidal crystalline phase in which the system displays iridescent colors.

GG6.43

Dispersed in an aqueous solution, gold nanoparticles can self assemble into films at the liquid-air interface when another solvent is introduced into the solution. Many approaches have been reported for forming self assembled nanoparticle films in solution, but most of them involve the modification of nanoparticle surfaces before the film formation process. Here, as an example, coating the nanoparticles with alkanethiols will reduce the solubility of the nanoparticles in water and drive them to the liquid-air interface to form two-dimensional films. In this presentation, we demonstrate a new approach for the self-organization of gold nanoparticles at the liquid-air interface. This approach does not require the extra step for the modification of the gold nanoparticle surfaces. Gold nanoparticles, with sizes from 5 nm to 100 nm, are directly synthesized in an aqueous solution. A second solvent is then introduced into the solution in a carefully controlled fashion. The originally well-dispersed gold nanoparticles will self-assemble into two-dimensional films at the liquid-air interface. When transferred onto solid substrates, these films are ideally suited as substrates for surface enhanced Raman spectroscopy (SERS). Compared to SERS active nanoparticles suspended in solution, these solid thin film substrates can sustain the change of pH, solvents, etc., in the detection process using SERS. When they are exposed to gaseous target molecules, these thin films can also give intense Raman signal.

SESSION GG7: Micro- and Macro-assembly Strategies Chairs: James Hutchinson and Gerard Wong Wednesday Morning, December 1, 2004 Room 311 (Hyatt)

8:30 AM *GG7.1 Directed Assembly of Materials from Nanoscale Building Blocks. Richard W. Siegel, Rensselaer Nanotechnology Center and Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York.

Great strides are now being made in our ability to assemble nanoscale building blocks to create advanced materials with novel properties. A perspective of this area in materials research will be presented based upon experiences from our work in the Center for Directed Assembly of Nanostructures supported by the National Science Engineering Initiative of the U.S. National Science Foundation. The presentation will include examples of directed assembly of nanoparticles, nanorods, and hybrid structures containing these and biomolecules to make new materials with enhanced mechanical, electrical, optical, and bioactive properties, and multifunctional combinations thereof. The opportunities and challenges facing the specific field of research community in moving forward in this area will be considered.


Size dependent optical, electronic, and physical properties of nanoparticles, nanorods and nanowires not only depend on their dimensions but also critically depend on their assembly. It is known, for example, that surface plasmon absorption of a metal nanoparticle is different in the case of an isolated particle, a particle within a chain and a particle in a two-dimensional lattice. Among all the nanomaterials monolayer protected metal-nanoparticles (MNP) are particularly interesting because chains that compose their ligand shell, it is not only possible to change and control the overall material properties, but also to induce given surface properties. Here we show how recently discovered mixed monolayer protected nanoparticles, that showed ordered domains in the ligand shell,[1] can be chemically modified in specific equatorial spots of their chain. By placing in such spots molecules that have chemically reactive end groups it is possible to induce the assembly of nanoparticles in a controlled fashion. For example, by placing two carboxylic acid terminated molecules in diametrically opposed position on a nanoparticle, and by reacting such particles with diamine terminated molecules it is possible to generate long chains of nanoparticles. Control over the numbers and relative position of the molecules placed on the nanoparticles enables us to produce chains, rings and other shapes of particles. Alternating amino functionalized and carboxylic acid functionalized nanoparticles allows the synthesis of chains of alternating types of particles, e.g. silver/gold chains. Chains of nanoparticles with cores bigger than 15 nm with a core to core distance of 3nm are potential candidates for use in surface enhanced Raman spectroscopy (SERS). Indeed preliminary results in this direction will be discussed. 1 A. Jackson, J. Myerson, and F. Stellacci, Nature Materials 2004, 330.


Dielectrophoresis, particle polarization and mobility in alternating electric fields, allows manipulation and controlled assembly of colloid particles. We use electric fields to make particle into direct planar microarrays above planar on-chip electrodes and to interface them with electrical circuits. We will report how microparticles, nanoparticles and live cells can be assembled in 1D chains and 2D arrays by the use of AC fields. The simplest type of particles that we have studied is dielectric latex or silica microspheres. The combination of dielectrophoresis and dipolar chaining leads to the formation of single-domain centimeter sized photonic crystals with specific orientation. Such electrically switchable crystals act as rudimentary photonic antennas for studying the interactions and phase transitions in particle ensembles. Dielectrophoresis can also be used to assemble metallic nanoparticles into electrically conductive microcircuits. The dynamics of the process can be modeled, and the microwire growth direction can be steered to make self-assembled “wet” circuits. The natural extension of these principles is the assembly of live cells. Chains and membranes from yeast cells were prepared between electrode pairs and the optimal conditions in terms of field and frequency will also demonstrate how by balancing the induced dipole interactions the process can be extended to co-assembly of cells and synthetic particles. The biocomposite arrays obtained by dielectrophoretic assembly techniques can be used as components of sensors and microreactors.


Diel (834)

Here we present several lithographic approaches that we have adopted to fabricate nanopatterned polymer brushes. We demonstrate the use of nanoshaving, where an atomic force microscope (AFM) cantilever tip is employed as a nanomechanical tool to selectively remove a thiol resist. The freestanding gold surface in the resulting nanopattern was immediately backfilled with a bromo-thiol initiator and enabled patterned surface-initiated polymerization (bottom-up) from immobilized thiol initiator. The resulting patterns are then amplified by surface-initiated polymerization (top-down) from immobilized thiol initiator. We demonstrate that by choosing an appropriate nanolithography technique and combining it with a suitable polymerization technique allows us to fabricate high-density polymer brush arrays with control over chemical functionality, feature dimension, shape, and interfeature spacing on the nanometer length scale. We believe that we are the first to show that brush height depends sensitively on the size of the characteristic dimension of the initiator nanopattern. This behavior potentially has significant consequences for the design and fabrication of nanopatterned polymer brushes. Furthermore we demonstrate that the spatially controlled immobilization of stimuli-responsive macromolecules on nanopatterned surfaces at the nanometer length scale enables fabrication of smart externally switchable polymer nanoarrays. Such nanostructures can provide sensing functionality within integrated nanoscale bioanalytical devices in which the transport, separation, and detection of biomolecules must be performed in aqueous solutions.

10:00 AM *GG7.8 In-situ Synthesis and Directed Assembly of Gold Nanoparticles of Different Shape from Spatially Constrained Surfactant Aggregates. G. Ramanath, Ashvani Kumna, Vivek Agarwal, Arijit Bose and Vijay John, Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

Here we present several lithographic approaches that we have adopted to fabricate nanopatterned polymer brushes. We demonstrate the use of external reducing agents and open up new possibilities for realizing materials filled with organized assemblies of nanomaterials. Metal nanoparticles exhibit unique shape dependent optical properties such as enhanced fluorescence in gold nanorods and quadrupole plasmon resonances in silver nanocrystals, making them attractive for optical nanodevice concepts and applications. A number of protocols have been developed to modulate the nanoparticle shape. While most protocols result in predominantly rod-like nanoparticles or nanofibers of variable aspect ratios, faceted morphologies, e.g., triangular or flat hexagonal particles have been observed less frequently. Here, we synthesize faceted gold nanoparticles without using any external reducing agents such as citric acid or sodium borohydride. Adding an aqueous gold chloride into a AOT/Lechithin/brij98 toluene mixture results in gelation and formation of spatially constrained micromasculations of different shapes depending upon the water content. The charged surfactants in the constrained environment reduce gold ions, and serve as capping agent, resulting in nanoparticles of triangular or hexagonal shapes. The nanoparticles and their assemblies have been characterized by cryo- and conventional transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transforms infrared spectroscopy (FTIR), UV-visible Spectroscopy and Nuclear magnetic Resonance (NMR) spectroscopy. Based upon our measurements, we propose a phenomenological model to describe the relationship between the synthesis and assembly process parameters and particle shape and assembly structure.


We have developed a novel approach to patterning 3D periodic mesostructures via direct-write assembly of nanoparticle and polyelectrolyte inks. Central to our approach is the creation of nanoscale patterns using a 3-axis controlled robotic nanolithography system. These nanoscale mesostructures may find potential application as functional and structural composites, or templates for photonic materials and sensors.

11:00 AM *GG7.7 Smart Nanostructured Materials by Sequential Layering: From Photonics to Ultrastrong Material and Tissue Engineering. Nicholas Alexander Kotov, Chemical Engineering, University of Michigan, Ann Arbor, Michigan; Biomedical Engineering, University of Michigan, Ann Arbor, Michigan.

Layered nanocomposites with high degree of organization can be prepared from polymers and a variety of nanocolloids such as nanoparticles, nanowires, nanotubes, clay platelets, and proteins by means of a new thin film deposition technology known as layer-by-layer assembly (LBA) and self-assembly of surfactants into multilayers. The organic and inorganic materials are deposited in regular stacks determined by the deposition protocol. Control of distance and orientation of nanocolloids in the multilayers affords fine-tuning of the composite properties - optical, electronic, mechanical and biological. Recent examples of nanocomposites with unique characteristics include photoactive thin films from nanoparticles, and ultrastrong materials from single wall carbon nanotubes (SWNT), carbon fibers, and clay platelets. Immobilization of the SWNTs in the composite in each deposition cycle prevents phase separation and makes the distribution of the nanotubes highly uniform. The successful deposition of the multilayers with complex nanostructures can also be extended toward biological applications, which include implantable sensors and artificial tissues.

11:45 AM GG7.9 Microemulsion-Based Synthesis of Stacked Calcium Carbonate (Calcite) Superstructures. Chulanapa Viravaidya, Mei Li and Stephen Mann, Chemistry: Inorganic and Materials department, Bristol university, Bristol, United Kingdom.

The synthesis of organized extended structures based on the assembly of nanostructured building blocks is currently recognised as an important theme in the nano-micro interface. Complex macroscopic structures consisting of self-organized surfactant-inorganic nanocolloids of BaSO4, BaCrO4, BaCO3, CaSO4, or CaCO3 can be synthesized in water-in-oil microemulsions by emergent processes involving nucleation and growth within aggregates of surfactant-coated amorphous inorganic nanoparticles. Recent studies on calcium carbonate crystallization in microemulsions have shown that different polymorphs with higher-order complex architecture can be prepared by changes in the reactant molar ratio, number ratio of water droplets per nanoparticle (n), and size of the microemulsion water droplets as defined by the = H2O/phosphate value. In this communication we report the spontaneous formation of novel complex architectures of the thermodynamically stable calcium carbonate polymorph, calcite, by addition of sodium carbonate in each microemulsion NAOFT microemulsions (w = 40) to reverse micelles of calcium dodecylbenzenesulfonate under conditions of high alkalinity (pH = 11) and Ca++ : CO3 results revealed that the precipitated material consisted of stacked arrays of ca. 20 nm-thick plate-like calcite crystals with pseudo-hexagonal morphology. Significantly, high magnification SEM images showed close morphological alignment of the plates, suggesting the presence of strong interparticle contacts between adjacent lamellae. Electron diffraction also indicated some degree of crystallographic preference between the adjacent lamellae. Patterns recorded from stacks that consisted of less than four well-defined plate-like lamellae and viewed end-on showed either a single [001] zone pattern or a superposition of [001] zone patterns that were very closely aligned with an angular
deviation of less than 10°. The data were therefore consistent with a novel proof-of-concept demonstration. For example, synthetic chemistry now provides the possibility of designing molecular and nanocolloidal building blocks of matter with anisotropic interactions due to anisometry, functionalization, or surface patterning. Genetic and molecular engineering of biomolecules and macromolecules has opened up new possibilities for conferring recognition and chemical specificity to inorganic nano building blocks. Principles of self-organisation in living systems are being exploited for the assembly of synthetic structures from biologically-inspired building blocks. However, in contrast to traditional materials, little is known about the properties of these new building blocks, the forces between them controlling their assembly into target structures and bulk phases, and the properties of these assemblies. We seek to develop a theoretical framework for predicting the self-assembled structures that result from nano building blocks patterned or functionalized with organic and biomolecule ligands. In this talk, we present results of molecular simulations and Monte Carlo simulations of self-assembly of model patterned building blocks, and show how building block shape and topology, pattern anisotropy, and recognition interactions can be exploited to achieve complex mesoscale two- and three-dimensional structures such as wires, sheets, junctions and shells [1-4]. We apply geometric packing rules and discuss their opportunities and limitations for predicting equilibrium structures. We investigate how assembly thermodynamics and kinetics and explore transformations between ordered structures under changes in thermal and external fields. We further investigate via simulation the stability of assembled structures with respect to various fabrication limitations of the building blocks [5], for applications to nanoelectronics, nanocomputation, storage. [1] Z.L. Zhang and S.C. Glotzer, Self-assembly of patchy particles, Nano Letters, accepted. [2] Z.L. Zhang, M.A. Horsch, M.H. Lamm and S.C. Glotzer, Tethered nano building blocks: Toward a conceptual framework for nanoparticle self-assembly. Nano Letters, 2003. 3(10): p. 1341-1346. [3] Z.H. Chen, M.H. Lamm and S.C. Glotzer, Monte Carlo simulations of biomolecular-directed assembly of nano building blocks, J. Chem. Phys. 119 (2003) 11048-11055. [4] M.A. Horsch, D.J. Jacobson, Z.L. Zhang, and S.C. Glotzer, preprint. [5] S.L. Teich-McGoldrick, Z.L. Zhang and S.C. Glotzer, preprint. This work is supported by grants from the NSF (CTS-0210551), and the DOE (DE-FG02-02ER46000 and DE-FG02-03-ER46004). 1:45 PM **GG8.2** Computational Studies of Anatase Nanocrystals, Serban Erdinç, Amanda B. Barnhart, and J. Woods Faculty 1Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois; 2Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; 3School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota. Titanium oxide nanoparticles and their assemblies have attracted a lot of interest due to their potential in photochemical applications. The theoretical modeling of nanoparticle units is a computational challenge because the systems of interest are not periodic and not small, typically having 10^4 atoms or more. A self-consistent tight-binding (SCTB) method could be used to treat systems of this size has been parameterized for anatase and applied to a faceted anatase nanoparticle of the size of about 1 nm (105 atoms). The results have been compared for structure relaxation of the same nanoparticle performed by density functional theory. Optimized geometries at both levels of theory show good agreement. We have also compared results on nanoparticle cohesive energies and electronic charge distributions. For the latter, we have performed calculations of both electron density and electronic localization functions in the density functional study. Following validation of the results, larger nanoparticles (2 - 3 nm) were studied using tight binding methods. These units are suitable for studies of the assembly processes molecular dynamics simulations, which will help to understand properties of anatase-based nanoarchitectures. 2:00 PM **GG8.3** Plastic to Superconducting Properties of Silicon and Carbon Nanostructured Clathrates, Xavier Blase, Laboratoire de Physique de la Matière Condensée et des Nanosciences, CNRS and University Lyon I, Villeurbanne, France. Column-IV semiconducting clathrates are nanostructured crystals composed of face sharing clusters. Therefore, in such systems, the building unit is not the atom but small semiconductor cages. While all atoms are in the fourfold sp³ hybridization, as in the diamond phase, the cage structure induces the presence of a large number of pentagons in the network and the possibility of endohedral doping (or intercalation) by placing atoms at the center of the cages. Such a unique topology induces origin properties that are not met by any ab initio techniques. It is shown in particular that: a) endohedral doping of silicon clathrates can open a direct band gap in the visible range (from 1.9 to 2.4 eV, GW value), opening the way to an all-integrated silicon-based opto-electronic technology [1], b) the observed 8 K superconductivity in baryum doped Si-clathrates is found to be an intrinsic properties of the sp³ silicon network. The electron-phonon (e-ph) coupling is strong (A = 1) and, in the case of the carbon clathrates, the e-ph coupling potential is shown to be much larger than in the fullerenes [2]. The strength of the e-ph coupling in carbon-clathrates, doped-diamond and small radius nanotubes are compared. c) the ideal strength of the carbon clathrates is shown to be superior to that of diamond in its "weak" <111> tensile or shear directions due to the frustration of the diamond-to-graphite instability by the clathrate cage-like structure [3]. This provide a first explanation for the repeated observation that cage-like carbon materials, such as polymerized fullerenes, cage-like carbon nanotubes and provide new criteria for realizing ultra-hard materials. [1] D.Connetable, V.Timoshevskii, E.Artacho, X. Blase, Phys. Rev. Lett. 87, 206405 (2001) [2] D. Connetable et al., Phys. Rev. Lett. 92, 215505 (2004) [3] X. Blase, Philippe Gillet, A. San Miguel, and P.Melmon, Phys. Rev. Lett. 92, 215505 (2004)
Materials Science, University of Illinois, Urbana, Illinois.


4:00 PM *GG9.2
Microstructure Evolution and Materials Synthesis in a Self-Assembled Mixed-surfactant Mesoporous, Arijit Bose
1Chemical Engineering, University of Rhode Island, Kingston, Rhode Island; 2Chemical Engineering, Tulane University, New Orleans, Louisiana; 3Chemistry, Tulane University, New Orleans, Louisiana.

Soft nanoscale materials, such as micelles, vesicles, microemulsions, liquid crystals and other complex fluids are becoming increasingly important from both a scientific as well as technical applications perspective. Visualization of these materials is a challenge because of their size (2 to 100 nm), their low electron density and because their aggregation state and morphology is critically dependent on solvent evaporation. Soft nanoscale materials will be provided. These include reciprocal space imaging using Small Angle Neutron Scattering (SANS), as well as direct imaging using cryogenic Transmission Electron Microscopy (cryo-TEM) and Freeze Fracture Direct Imaging (FFDI). Advantages and limitations of each of these techniques, as well as how they complement each other, will be discussed. A novel transformation from a microemulsion to a gel phase has been observed by increasing the water content of a system consisting of AOT and lecinthin in isooctane. Small angle neutron scattering (SANS) patterns are consistent with models that describe the microstructure as columnar hexagonal at lower water contents and temperatures, and lamellar at higher water content and temperature. The structures can be aligned using shear, are thermally reversible, and have been used as robust templates for a variety of reactions in the aqueous and organic nanochannels. The morphology of the nanostructured phases mimics the underlying structure of the surfactant aggregates. This feature opens up many opportunities for template-directed materials synthesis, and several examples will be shown.

4:30 PM GG9.3

Mixed solution of surfactant (Alkylamine (AA)) and metal-alkoxide (MA) was contacted with water. Lamellar structure composed of surfactant and ceramic oxide was formed at the liquid-liquid interface, and ceramic nanosheet such as TiO2, SiO2, and GeO2 was synthesized. These nanosheets were characterized by transmission electron microscope images, selected area electron diffraction (SAED), and X-ray diffraction (XRD). XRD and SAED results showed that GeO2 nanosheet had tetragonal crystal, which confirmed to the square shape of GeO2 nanosheets. In situ small angle X-ray scattering measurement was carried out every second for several minutes using strong X-rays by synchrotron radiation in the SPRing 8, and the formation processes of ceramic nanosheet was examined. When the mole ratio of Ge(OE)4 to MA was adjusted to 0.2, the peaks corresponding to lamellar phase appeared at 2.5 sec after contact and increased with time. The periodical distances of the lamellar phases were almost constant, from 3.6 nm to 3.8 nm, which corresponded to the thickness of bilayer composed of surfactant molecules. The peak shape of the lamellar phase in SAXS measurement changed from 100% Gaussian distribution at 2.5 sec to 100% Lorentzian distribution after 28 sec to 180 sec from contact. These findings indicate that high crystallized ceramic nanosheets can be synthesized when the suitable surfactant molecule was chosen.

GG9.4
Gold Nanoparticle Assembly Within Soft Linear Templates, Robert G. Shinnin, Lori K. Sanders, Gerard C. W, Long and Paul V. Braun; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Gold nanoparticles, 2 nm in diameter, have been assembled along or within a variety of linear templates. To facilitate their assembly they have been functionalized. The systems studied include quaternary ammonium modified gold, which assembles along the negatively charged, rodlike biomolecule actin; naphthenic acid-modified gold, which assembles within the cylindrical hydrophobic domains found in the hexagonal phase lyotropic liquid crystals produced by some water-oil surfactant ternary mixtures. We have used small angle X-ray scattering to probe the structure of these templated gold nanoparticle assemblies, addressing issues such as the effect of the nanoparticles’ presence on the template’s structure, the inter-nanoparticle spacing along or within the linear template, and the ability to form close-packed nanoparticle arrays. In systems where the nanoparticle surface chemistry permits interparticle cross-linking, we have exposed the nanoparticle-doped templates to such cross-linking treatments, and we contrast the results of such experiments to the cross-linking of the same gold nanoparticles in unstructured solution.

SESSION GG10: Poster Session: Mesoscale Architectures from Nanounits: Assembly, Fabrication and Properties II

Chairs: Paul Braun, G. Ramanath and Mauricio Teran

Wednesday Evening, December 1, 2004
8:00 PM
Exhibition Hall D (Hynes)

GG10.1
Mesoporous Carbon/Silica Composite with Alternating Carbon-Silica Layers Integrated at a Molecular-Scale in the Pore Wall, Jiebin Fang and Yungfei Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Mesoporous silica is of great interest for many applications. Functionalization of mesoporous silica, a process that imparts functionality to the pore surface or wall, is essential to convert the relatively inert silica into various functional materials. Up to date, functionalization of mesoporous silica is often achieved by post-grafting methods, direct synthesis methods, or by using functional surfactants. The direct synthesis method provides mesoporous silica with functionalities through co-assembling surfactants with organosilane precursors that contain non-hydrolysable pendant or bridged organic ligands. However, current research in this area has been focused on the synthesis of functionalized mesoporous silica with organic or metalic moieties. This work reports the synthesis of ordered mesoporous carbon/silica composites with unique pore walls that are composed of molecularly integrated layers of silica and carbon. This is achieved by co-assembling octadecyltrimethylsiloxyl bromide (OTAB) with 1,4-bis-(trithoxysilyl)-benzene (BTEB), followed by a carbonization process that decomposes the surfactant and converts the phenylene moieties into carbon. The materials were characterized by X-ray diffraction (XRD), nitrogen and hydrogen sorption isotherms, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and other techniques. The incorporation of carbon layers into the pore wall not only results in interesting mesoporous carbon/silica
nanocomposites with meso- and molecular-scale order, but also may provide materials with improved thermal, chemical, and mechanical properties. Furthermore, removal of the silica from the carbon/silica nanocomposites results in mesoporous carbon with positively replicating mesostructure. Compared with the current two-step templating synthesis of mesoporous carbon, this method provides a direct method to reproduce ordered mesoporous carbon for hydrogen storage (e.g., 1.2 wt % at ambient pressure and 77 K), catalysts, fuel cells, and other applications.


Recent experiments have shown arrays of polymeric ridges or gratings developed from a droplet of oil dispersed in water and sandwiched between two glass wafers. The ridges form as the wafer separates under tensile forces. We will report on our efforts to characterize this process and the resulting gratings. The ridges only form when the bulk glass transition temperature of the polymer is greater than the temperature of the wafer. The ridge density is determined by the ratio of water to oil in the dispersed phase. The period of the gratings is set by the ratio of the oil and water volumes.
applications in separation science or serve as catalysts with nanoparticle properties in ordered, micron sized aggregates.

GG10.7 A Novel Mediator-Template Assembly Route Towards Size- and Shape-Controlled Nanoparticle Assemblies.

Mathew M. Varghese1, Stephanie Wu2, Yanxia Lin1, Jin Lou1, Zia Bab1, Navaid Khan1, Daniel Rabinoovich2, Tianbo Liu3 and Chuan-Jian Zhong2.


The ultimate exploration of nanoparticles in nanoelectronics, information storage, quantum computation, and chemical/biological sensors will depend on the ability to precisely assemble nanoparticle complexes in controllable patterns with well-defined interparticle spatial properties. This presentation focuses on our recent findings of an investigation in this direction focusing on mediator-template assembly via multidentate thioether ligands. We have developed an effective mediator-template assembly strategy that can assemble gold nanoparticles into three-dimensional assemblies of controllable sizes (40-300 nm) and shapes. This strategy explores novel size- and shape-driving forces exerted by tetraalkyloxalimmonium bromide template shells and multidentate thioether mediators. The assembly processes have been characterized in-situ by spectrophotometric, dynamic light scattering, and x-ray diffraction techniques. The morphologies have been probed by atomic force microscopy and transmission electron microscopy. Potential applications of the nanoparticle assemblies in sensors, catalysis, and nanoelectronics will be also discussed.

GG10.8 Periodic Array Nanostructures Using Colloidal Particle Lithography, Hyunjung Shin1, Changdeok Bae1, Jooho Moon1 and Myung M. Sung2.

1School of Advanced Materials Engineering, Kookmin University, Seoul, South Korea; 2Department of Chemistry, Kookmin University, Seoul, South Korea; 3School of Mechanical Engineering, Yonsei University, Seoul, South Korea.

In this work, we demonstrated a new preparation method of nanostructured carbon materials, including periodic array surface patterns in self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) by two-dimensional (2D) crystalline structure of colloidal particles, selective atomic layer deposition (ALD), and chemical etching. Periodic array patterns of OTS - SAMs were prepared by immersing of the Si substrate with 2D crystallized colloidal particles in anhydrous toluene solutions containing OTS molecules. Size of the periodic array patterned holes in OTS - SAMs was estimated by simple geometrical calculation to be 45 nm, 59 nm, and 70 nm when SiO2 colloidal particles of 200 nm, 346 nm, and 500 nm in diameter, respectively, and OTS - SAMs (estimated thickness of 2.5 nm) are used. Experimental results showed the size of about 51.6, 78.7, and 93.7 nm, respectively, by atomic force microscopy (AFM). The estimated pattern size was achieved through the removal of the confined liquid in capillary between the colloidal particle and the substrate. Selective deposition of TiO2 by ALD onto the patterned OTS - SAMs by using hydrofluoric acid allows to fabricate the periodic array of isolated nanostructures in sub - 100 nm scale. This novel process can serve as an alternative method to fabricate nanopatterns and nanostructures.

GG10.9 Low Temperature Coalescence of Colloidal Gold Multilayers to Form Conductive Films. Lakshmi Supra1 and Richard O. Claus2.

1Macromolecular Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia; 2Fiber & Electro-Optics Research Center, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Gold films were fabricated on glass and a flexible polyimide, Kapton; by a solution-based assembly process using linker molecules. The substrates are modified by an amine-terminated silane and subsequently dipped in colloidal gold solution. The multilayers were built up by dipping the gold coated substrate alternately in a solution of 1, 6-hexanethiol and colloidal gold solution. The resistance of the films after the deposition of 10 bilayers was ca. 1 MΩ. The films were heated at 3 different heating temperatures, 20°C, 60°C, and 100°C for different lengths of time. The resistance of the films decreased dramatically with increasing time of heating, and after 12 h a lowest resistance of 40 Ω was obtained. The decrease in resistance occurred five orders of magnitude at lower temperatures. X-ray photoelectronic spectroscopy revealed a decrease in the intensity of the S 2p peak from the dithiol, with increasing time of heating. Atomic force microscopy and scanning electron microscopy images of the samples showed a coalescence of the gold colloids, leading to increased conductivity. The coalescence occurs due to a thermal desorption or degradation of the dithiol linker molecule. The thermal desorption of thiols from gold surfaces has been observed before, but not for multilayer film of gold particles. This method paves a way for low temperature thermistor type switches on flexible materials. Another potential application is the patterning of the films by lasers, by selective heating, to form regions of different resistances for use in flexible electronics.


1Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana; 2Institute of Physics, Chinese Academy of Sciences, Beijing, China.

In recent years, there has been a great interest in the synthesis of mesoporous carbons because of their unique structures and properties. Various methods of mesoporous carbon materials have been fabricated using a complicated templating synthesis method. This method allows precise pore-size control through replicating the mesostructure of the silica templates. However, the complicated multistep synthetic procedures hamper the practical applications of these mesoporous carbons. Surface functionalization is a fundamental method for the application of carbon materials in catalysis and environmental process. Although the modification of activated carbon and carbon nanotubes is well known, the functionalization of mesoporous carbon materials has been less investigated. In this work, mesoporous carbon with high surface areas, large pore volumes, and narrow pore size distributions was synthesized using low-cost sucrose as carbon precursor by a simple one step sol-gel technique followed by carbonization and template removal. The pore diameter of the mesoporous carbon is about 2.2 nm and the surface area is larger than 2000 m²/g. In order to explore a suitable functionalization condition, the mesoporous carbon was chemically modified using HNO3 with different concentrations followed by SOC12 treatment and then reacted with the chemicals with different functional groups. In this study, nitrogen, phosphorous-containing ligands and sulfur, nitrogen-containing groups were successfully introduced to the surface of mesoporous carbon materials. The materials were characterized by nitrogen sorption, TEM, FTIR and NMR. The functionalized mesoporous carbon materials may have potential applications in catalysis and environmental process, such as preparation of organometallic catalysts and selective adsorption of heavy metals.

GG10.11 Using Surface Forces to Create Nanoscale Electrochemical Junctions, Steven M. Tobias1, Jennifer Giocondi1, Dong-Wan Kim1, W. Douglas Moorehead2, Sung-Yoon Chung3 and Yet-Ming Chiang1.

1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2US Navy, Virginia Beach, Virginia; 3Inha University, Incheon, South Korea.

The anticipated size reduction of electrochemical devices such as batteries, capacitors, electrochromics, and sensors down to the micro- and nanoscale can benefit greatly from device junctions that are "self-organizing" rather than requiring the deliberate deposition or insertion of electrolytic layers. In this work we study the use of surface forces such as the repulsive van der Waals force to form such junctions. We use measured thermodynamic and spectroscopic data to select relevant material systems. The materials selection process includes calculations using frequency-dependent optical properties to determine the sign and magnitude of the vdW interaction and other surface forces between dissimilar conductive solids such as metals, graphite and conductive oxides, separated by organic solvents or polymers. Atomic force microscopy (AFM) is used to measure the interaction between single particles and between particles and films. For the first time, repulsive vdW forces have been demonstrated between electronically conductive materials capable of forming device junctions. Cyclic voltammetry is used to characterize the stability of the junctions at potentials relative to devices such as capacitors and lithium ion batteries. This approach is expected to be applicable to nanoscale junctions formed between colloidal particles and films in a variety of device geometries.


1School of Chemistry, SUNY-Binghamton, Binghamton, New York; 2Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

In the past decade, mesoporous TiO2 has attracted more and more attention because of its wide applications in photocatalysis, solar cell, chemical sensors, etc. However, compared with the sol-gel chemistry of silicon alkoxide, combination of transition metals (TMs) sol-gel chemistry with templating approach is more difficult to master due to the fact that sol-gel reactions of transition metal alkoxides are much more complex. In this work, two templating approaches were applied to synthesize mesoporous TiO2 particles. The results confirmed the feasibility of both approaches. The first one was using aerosol-assisted co-assembly technique. This was achieved by atomizing TiO2 sols containing...
homogeneous TiO$_2$ precursor and colloidal silica template. During the aerosol process, solvent evaporating from the droplets enriched the nonvolatile components and resulted in co-assembly of TiO$_2$ and colloidal silica into spherical particles. Subsequent crystallization of TiO$_2$ and removal of colloidal silica resulted in mesoporous anatase TiO$_2$ particles. The second route to the synthesis of mesoporous TiO$_2$ was using one-pot hydrothermal treatment (THC) in the presence of surfactant (e.g., F127) under hydrothermal condition in absolute ethanol, resulting in mesoporous crystalline structure. Mesoporous anatase TiO$_2$ particles were obtained through this one-pot method and used as a support for the growth of supported catalysts, as the light-off curve shifted to high temperature.

By using this layer-by-layer approach, one layer of a high- isoelectric metal-alkoxide species to regenerate surface hydroxy Is. The one-layer approach for the fabrication of metal-oxide nanomaterials usually require functionalization of a relatively inactive silica surface through the reaction of a high density of silanol groups with organic functional groups or incorporation of mesostructured non-siliceous solids has extensively exploited. Herein, we applied a hydrolytic surface sol-gel process, a technique developed by Frenkel and coworkers to fabricate metal oxide films with thickness control to nanometer precision on a flat substrate, on the modification of the surface properties of mesoporous silica materials. This technique consists of two half-reactions: (i) non-aqueous condensation of metal-alkoxide precursor molecules with surface hydroxy groups, and (ii) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxy groups. The one-layer film growth is achieved by repetition of saturated adsorption of metal-alkoxide precursor molecule on preformed oxide layer often by diffusion or forced injection. These mesoporous anatase particles are of great significance for photocatalysis and other applications.


Since their discovery in 1992, silica-based mesoporous materials have attracted intense interest because of their potential applications in catalysis and separations. However, most applications of these mesoporous materials usually require functionalization of a relatively inactive silica surface through the reaction of a high density of silanol groups with organic functional groups or incorporation of mesostructured non-siliceous solids has extensively exploited. Herein, we applied a hydrolytic surface sol-gel process, a technique developed by Frenkel and coworkers to fabricate metal oxide films with thickness control to nanometer precision on a flat substrate, on the modification of the surface properties of mesoporous silica materials. This technique consists of two half-reactions: (i) non-aqueous condensation of metal-alkoxide precursor molecules with surface hydroxy groups, and (ii) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxy groups. The one-layer film growth is achieved by repetition of saturated adsorption of metal-alkoxide precursor molecule on preformed oxide layer often by diffusion or forced injection. These mesoporous anatase particles are of great significance for photocatalysis and other applications.

GG10.14 Control of Molecular Orientation of Phthalocyanine Films by using Ultrathin 3,4,9,10-Perylene Tetracarboxylic Dianhydride Template Layers. Takeaki Taniguchi, Shunsuke Kamata and Hideki Naoe; Konan University, Kobe, Japan.

Ligand-protected nanoparticles consisting of semiconductor cores surrounded by organic monolayers have attracted considerable interest for applications in nanomaterials science and nanotechnology. The organic surroundings can provide stability and additional functionality to the nanoparticles. Thin films of particular interest for the development of novel devices that utilize the specific characteristics of semiconductor nanoparticles. The development of a method that allows effective surface modification of semiconductor nanoparticles with diverse surface functionalities would be extremely beneficial for the development of electrical and optical devices using these semiconductor nanomaterials. In this study, we report an experimental investigation of surface chemical modifications of CdS nanoparticles in order to form mixed monolayer-protected nanoparticles, along with a covalent bonding-based layer-by-layer approach for the fabrication of nanocomposite films on glass substrates. CdS nanoparticles initially prepared using the reverse-micelle method were used to modify nanoparticle surfaces with 1-decanethiol molecules by ligand exchange. Subsequently, 11-mercapto-1-undecanol was partially incorporated into the nanoparticles. The obtained mixed monolayer-protected nanoparticles were successfully immobilized on a grass substrate through a carbamate bond-forming reaction that could be further utilized for multilayer construction in a layer-by-layer fashion.

GG10.15 Architecture of Multi-Layered and Multi-Structured Mesoporous Silica Thin Films by Multi Spin Coating. Ji-In Jung, Jae Young Bae and Byeong-Soo Bae; Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea.

The mesoporous silica thin films with ordered pore structure are promising materials in such applications as sensor arrays, nanoreactors, electronic and photonic function devices, low-electric conductive composites, and hosts for bioorganic and biotechnology. The mesoporous structures of thin films were controlled with the ratio of amphiphilic aliphatic surfactant and tetraalkxoyxilane. They were synthesized by an evaporation-induced self assembly process and applied on Si wafer. A commonly used high performance evaporator evaporates excess solvents and decomposes surfactants produced
structurally stable mesoporous silica films. Mesoporous silica films with different pore sizes ranging from 2 to 10 nm and mesopore wall thickness ranging from 1 to 5 nm were prepared by using different surfactants. Through multi spin coating, we made multi-layered thick films of the same pore surface property or multi-layered and multi-structured mesoporous silica films with different pore surface properties by choosing different pore sizes, pore structure, and hydrophilicity of pore surface. Well-organized multi-layered and multi-structured mesoporous silica films with periodically varying layer properties are applicable for optoelectronic devices, sensors, functional coating; and biological surfactant layers of nanoparticles silica films were well adhered without delamination on the bottom layers after calcination. Ordered mesoporous structures were formed on the preformed mesoporous silica films, regardless of the substrate or bottom layer. This multilayered mesoporous silica films provide well-controlled and ordered porous multi-mesostructures where each layer is deposited by multi spin-on process. The orientational and structural characteristics of multi-layered and multi-structured mesoporous silica films was investigated by XRD, SEM, TEM, X-ray cross-sectional images, we confirmed that the hexagonal mesostructured and multilayered films with different pore sizes of 3.5 nm and 7 nm were formed. Also, the different hexagonal/cubic mesostructured and multilayered films with different pore sizes of 3.5 nm and 10 nm were confirmed by TEM.

GG10.17 Bimetallic Nanoparticles: Preparation using Phase Transfer Method and the Study of their Properties. Shweta A. Shetty1, Sampath S2, Kamani Chattopadhyay1 and Revashanker Narayanan3; 1materials research centre, Indian institute of science, Bangalore, India; 2department of inorganic and physical chemistry, Indian institute of science, Bangalore, India.

Multi-metallic alloy nanoparticles show excellent catalytic, electronic and magnetic properties and synthesizing them is a field of extensive research. In this work alloy nanoparticles were synthesized in a two phase liquid-liquid system by phase transfer method using alkane thiols as capping agents. The evolution of alloy particles during synthesis is studied using transmission electron microscopy (TEM) to see whether they form core-shell bimetallic or partially segregated alloy or pure alloy structures in the nanoscale. The rules that govern these bi-metallic particles to go into these kinds of structures in the nanoscale were tried to find out using the TEM study. The work also includes the study of the properties exhibited by these alloy nanoparticles.

GG10.18 Electrospinning of Functional Nanofibers as Aligned Arrays and Functional Architectures. Jess Thomas McCann, Dan Li and Younan Xia; Department of Chemistry, University of Washington, Seattle, Washington.

Electrospinning has garnered much attention recently as it provides an inexpensive and simple way to manufacture large quantities of nanowires. This system is traditionally used to spin organic fibers due to the viscoelastic requirement of the solutions. We have recently extended this system to spin composite fibers. By co-spinning sol-gel precursors with a water-soluble polymer, we have been able to tune the viscoelastic properties of the solution and thus the uniform composite fibers with excellent size control down to tens of nanometers. We have also fabricated uniaxially aligned arrays of nanofibers. These structures could be stacked into structures for device fabrication. In addition, we have also devised a new two-capillary spinneret that is simple and easily manufactured in the lab. The use of this spinneret has allowed for the fabrication of hollow nanofibers with a good degree of morphological control. This poster will cover all these aspects, with a focus on the fabrication of functional architectures relevant to various nanoscale devices.

GG10.19 Electric-Field Assisted Assembly of ZnO Nanowire to Gabaric Field Effect Transistors. Liang-Yih Chen, Hsiao-Chiu Lin and Liangcai Wu; Nanjing University, Nanjing, China.

An electric-field assisted assembly technique is used to align ZnO nanowires on the interdigit electrodes to study their electrical properties. ZnO nanowires were synthesized by both furnace and hydrothermal methods. The nanowires were deposited on the interdigit electrode structures and then aligned in the 10 μm-wide electrode gaps by using alternating electric fields at frequency between 500kHz and 3MHz with field strengths between 103 and 104 V/m. SEM analysis showed that the nanowires aligned parallel to the electric field lines and electrically contacted with gold electrodes. The alignment along the electric field was due to the polarization of ZnO nanowire. The dielectrophoretic behavior of ZnO nanowires in microelectrode arrays have been studied as a function of frequency and applied field strength. The electrical characteristics of the nanowire thin-film transistors (NW-TFT) on the interdigit electrodes deposited on SiO2/Si substrates are being measured. By using this low temperature assembly process, the NW-TFT can be produced on various substrates including plastics.

GG10.20 Actively Controlled Self-Assembly of Colloidal Crystals by Electrocapillary Effect. Chun-Wen Kuo, Jau-Ye Shiu and Polin Chen; Research Center for Applied Sciences, Academia Sinica, Taipei, Taiwan.

Self-assembly is a commonly used strategy in synthesis and fabrication. One of the most economic routes for the fabrication of large ensembles of functional nanosystem is to utilize self-assembly to build up building blocks such as colloids, nanotubes and nanowires. However, if the functional nanostructures are to be assembled across many length scales within the integrated system, it is necessary to develop new tools for large-scale assembly of functional building blocks, for example, colloidal crystals. In general, it can be configured to produce other novel functional materials using self-assembly process when it is integrated with more sophisticated microfluidic system.

GG10.21 Self-Assembly of Gold Nanoparticles on Nanometer-patterned Surface. Kunji Chen, Yongjun Zhang, Xinfan Huang, Guangqi Han and Liangwei Wu; Nanjing University, Nanjing, China.

The self-assembly process of gold nanoparticles on nanometer-step-patterned Si surface and polished Si surface were investigated by the convective self-assembly method. The colloidal gold particles with diameter around 10nm were synthesized using a reduction of chloroauric acid (HAuCl4) with trisodium citrate and tannic acid, and ligated by dodecanethiol. The convective self-assembly method was used to deposit the colloids dispersed in benzene onto the substrates. The substrates were dipped into the solution vertically at room temperature. As the solvent evaporates, the gold nanoparticles were grown onto the substrates. SEM results showed that the configurations of the gold arrays depended on the surface morphology of the substrates. On the nanometer-step-patterned Si surface the steps play a critical role in the self-assembly process of gold nanoparticles. And the capillary force from the steps drives the particles to line along the steps. Therefore the particles tend to self-assembly into one-dimensional line structures when the solvent evaporates. For the polished Si substrate there is a little difference. The particles formed two-dimensional hexagonal superlattice without the directional confinement.

GG10.22 Self-Assembly of Low-Dimensional Nanoparticle Structures. Jinjin Xiao1, Shuangang Huang2 and Mark Revele1,2; 1Department of Physics, George Washington University, Washington, District of Columbia; 2Code 6363, Naval Research Laboratory, Washington, District of Columbia.

Low-dimensional nanoparticle structures are synthesized by two techniques designed to favorably control the self-assembly of colloidal self-assembly. In the first technique, evaporation-driven colloidal deposition, a vertically positioned substrate is partially immersed in a nanoparticle suspension, subject to evaporation at room temperature and atmospheric pressure. The interfacial forces within the meniscus region at the solid-fluid-air interface enable the adhesion of the suspended nanoparticles to the substrate. In this geometry, the horizontal orientation of the meniscus results in the formation of a nanoscale wire. Removing a small amount of each liquid will interrupt the deposition process and wire-formation will resume at a new location. Changing the timing and amount of each liquid withdrawal easily controls the width of and spacing between the wires. In a second technique, electrocapillary writing, a heated tungsten wire is pressed against the backside of a substrate floating on a
nanoparticle suspension, thereby imposing an localized ac field. Finite element calculations show that the electrode concentrates the electric field, leading to electrophoresis just below the placement of the tip. The tip is then moved horizontally across the substrate as nanoparticles are deposited following its motion. In this way, low-dimensional nanoparticle structures are written on the substrate. The structure of the resulting films is characterized by scanning electron microscopy and atomic force microscopy and this reveals that the deposited material forms 1D, 2D, and fractal structures. We also characterize by resistivity measurements the electrical properties of metallic nanoparticle films formed by these techniques. We anticipate that electrical interconnects can be formed between planar circuit elements using these deposition approaches.

GG10.24
Thermal and Mechanical Properties of PMMA/Silica Nanocomposites with Controlled Nanoparticle/Polymers Interface. Jin Xiao1, Jae-Mok Yi1, Seong Kwon Seol1, Jung Ho Je1, Yung-Chin Yang2 and Yeukuang Huw1, 2.
1Materials Science and Engineering, University of Science and Technology, Pohang, South Korea; 2Physics, Ewha womans University, Seoul, South Korea.

Nanotubes and nanowires of r-conjugated polyprrole (PPy) and poly(3,4-ethynediolxyloxythiophene) (PEDOT) were synthesized by using nanotemplates through electrochemical polymerization method. Dodecylbenzenesulfonylic (DBSA) acid or tetrabutylammonium hexafluorophosphate (TBAPF6) were used as dopant in electrolyte. Either a HF or NaOH solution was used to remove the aluminum oxide template after polymerization. From the TEM and SEM photographs, we observed the formation of tube with diameter of 50 nm to 200 nm, length of 50 nm, and wall thickness of 20 nm. The structure of the resulting films is characterized by scanning electron microscopy (HRTEM). Oriented Attachment is a dominant mechanism in early stage of crystal growth and subsequent microstructural development of BaTiO3 nanoparticles.

GG10.25

A means will be presented to produce nonporous hydrogels through block copolymer templating. Micellar solutions of block copolymers of poly(ethylene oxide) (PEO) and a degradable component are cross-linked in an aqueous beam to produce hydrogels. Degradation of the labile blocks opens pores in the gel that reflect the microstructure of the ordered micelle phase. SAXS and SEM studies of three of these materials before and after degradation show order on the scale of 1-100 nm. The labile units means to produce these hydrogels will be presented, along with studies of the effect of cross-linking conditions on hydrogel properties and mass-retention during degradation of the labile blocks. Experimental results suggest that macromolecular diffusion through the hydrogels should be less than an order of magnitude of that through the pores, opening possibilities for selective or responsive macromolecular transport in these gels. The resulting nonporous PEO hydrogels should have chemical functionality in the pore-bearing regions that provides a means to further chemical modification. In addition to experimental results, field-theoretic calculations of the block copolymer micelle structure will be discussed.

GG10.26
Synthesis, Characteristics, and Applications of Polyprrole and Poly(3,4-ethynediolxyloxythiophene) Nanotubes and Nanowires. Bohyun Kim1, D. H. Park1, D. S. Sul2, S. J. Lee2, J. M. Kim1, Jinsoo Jou3, Haeyong Kang2 and Won Kang2, 1Physics, Korea University, Seoul, South Korea; 2Physics, Ewha womans University, Seoul, South Korea.

Nanotubes and nanowires of r-conjugated polyprrole (PPy) and poly(3,4-ethynediolxyloxythiophene) (PEDOT) were synthesized by using nanotemplates through electrochemical polymerization method. Dodecylbenzenesulfonylic (DBSA) acid or tetrabutylammonium hexafluorophosphate (TBAPF6) were used as dopant in electrolyte. Either a HF or NaOH solution was used to remove the aluminum oxide template after polymerization. From the TEM and SEM photographs, we observed the formation of tube with diameter of 50 nm to 200 nm, length of 50 nm, and wall thickness of 20 nm. The structure of the resulting films is characterized by scanning electron microscopy (HRTEM). Oriented Attachment is a dominant mechanism in early stage of crystal growth and subsequent microstructural development of BaTiO3 nanoparticles.

GG10.27
Controlled PMMA Particles Assembly on Substrate by Synchrotron X-ray Using Dispersion Polymerization. Jin Xiao1, Jae-Mok Yi1, Seong Kwon Seol1, Jung Ho Je1, Yung-Chin Yang2 and Yeukuang Huw1, 2.
1Materials Science and Engineering, University of Science and Technology, Pohang, South Korea; 2Physics, Ewha womans University, Seoul, South Korea.

Controlled assembly of micro or nano sized polymer particles on substrate has a potential to be applied to micro electrical and mechanical devices. However, it is not easy to control assembly of particles in a manner of diverse size and/or density and further to specific local areas. In this work we first tried to fabricate the poly methyl methacrylate (PMMA) particles assembly on various substrates using synchrotron x-ray induced dispersion polymerization. Depending on the x-ray flux exposed on substrates which were immersed in the dispersion media, the size and/or density of the PMMA particles were able to be controlled on selective areas. Investigation by the growth of the height of PMMA particles on specific areas of substrates which were exposed with higher x-ray flux, resulting in lower size and/or density of the PMMA particles. Such obstruction effect on areas with higher flux was attributed to a negative potential barrier layer that might be formed by concentration gradient of hydrated electrons, which can be generated by the irradiation of x-rays on substrates in the solution. Based on the obstruction effect in higher flux zone, we were able to fabricate a well defined assembly of PMMA particles in a manner of diverse size and/or density just by using a patterned mask for controlling the x-ray flux.

GG10.28
Nanocrystal-doped polymer spheres as building blocks for coupled resonator optical waveguides. Bjoern Moeller1, Nicolas L.Thomas1, Mikhail Artemyev2 and Ulrike K. Woggon1, 1Physics, University Dortmund, Dortmund, Germany; 2Institute for Physico-Chemical Processes, Belgrade, Serbia; 3University of Minsk, Belarus.

Colloidal CdSe nanorods (NR) and nanodots (QD) are nanomaterials that received much attention in recent years. NRs, for example, emit highly polarized light and can be used as active optical material in laser devices and photonic structures. In this contribution we study Coupled-resonator microspheres of radius R, 2.27μm building blocks for coupled resonator optical waveguides. Unlike other types of optical waveguides, waveguiding in the coupled-resonator optical waveguide
The coupled microsphere cavities were prepared by impregnating polystyrene microspheres with a sub_surface layer of CdSe nanocrystals. To achieve the proper core-shell composition, the microspheres (<0.1% size deviation) have been pre-selected via their Mie resonances. The coupled cavities, arranged in linear chain or various two-dimensional geometries (photonic molecules) are studied by microphotonics and scanning electron microscopy (SEM), combined with polarization sensitive mode mapping. The spatial distribution and the dominant polarization type of both the weakly and strongly coupled cavity resonances excited by the nanocrystal emission are analyzed. Furthermore and especially, it has been observed that a nanocrystal positioned on an equatorial plane of a photonic molecule results in a weak coupling with no significant loss in the Q-factor while a nanocrystal on the bi-sphere axis excites strongly coupled bi-sphere modes with strong nanocrystal concentration in three points along the bi-sphere axis. Both experiment and theory show strong photon mode coupling with pronounced mode splitting as well as weak coupling with no significant loss in Q-factor depending on the emitter position and orientation. We show for the first time a three-resonator coupling without Q-factor degrading. [1] A. Yaniv, Yong Xu, R. K. Lee, A. Scherer, Opt. Lett. 24, 711 (1999). [2] U. Waggon, R. Wannemacher, M. N. A. C. Arroyo, A. Y. LeTourneau, A. V. Artemyev, Appl. Phys. B 77, 469 (2003). [3] B. Moeller, U. Waggon, M. V. Artemyev, R. Wannemacher, Appl. Phys. Lett. 83, 2686 (2003).

GG10.29 Electrostatic Assembly in Aerosol-Processing: Tailoring the Energy Release Rate of NanoEnergetic Materials
Soo H. Kim1,2 and Michael R. Zachariah,3,4 1Mechanical Engineering, University of Maryland, College Park, Maryland; 2Physics, National Institute of Standards and Technology, Gaithersburg, Maryland.

Nanostructured fuel/oxidizer composites are being looked upon as a possible approach to enhance energy release rates. We have developed a new method of locating the combustion zone within the composite material to enhance heat energy release. The associated nanocomposite energetic materials, composed of assembled fuel and metal oxide nanoparticles with significantly higher energy release rate. The method is based on electrostatically enhanced assembly to promote the preferential arrangement of fuel and oxidizer nanoparticles in the aerosol phase. Two unipolar chargers are employed to generate oppositely charged aluminum and iron oxide nanoparticles, which enhance the formation of intimately interconnected nanocomposite energetic materials. The results of TEM and STEM elemental mapping analysis indicates that the negatively charged aluminum nanoparticles are homogeneously distributed around positively charged iron oxide nanoparticles. The results of burning tests and thermal analysis using differential scanning calorimetry (DSC) showed that aluminum/iron oxide nanocomposite aerosol materials synthesized by electrostatic assembly had burning rates that are a factor of 10 higher than those produced by random Brownian coagulation.

GG10.30 Shape- and Orientation-controlled Synthesis and Orientation-ordered Superlattices of Spinell Ferrites Nanocrystals
Qing Song and Z. John Zhang; School Of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

The current intense researches on nanomaterials have been conducted due to their novel electronic, optical, magnetic, thermal, and mechanical properties. Recently, keen interests have been expanded into controlling the shape of nanomaterials and understanding the correlations between the material properties and its shape. The shape of nanomaterials can be as vital as the size in determining the uniqueness and novelty of material properties. Moreover, the assembly of nanometer unit building blocks is a key process in the design and construction of new nanostructures. The shape and related properties will be crucial for such assembly and device designs. Shape-controlled synthesis of nanocrystals is an experimental challenge. Shape control of nanocrystals have been achieved and reported in the syntheses of metals and semiconductors. Certainly, it is desirable to develop strategies for shape-controlled syntheses of complex metal oxides possessing rich properties, especially the magnetic characteristics. Here we present the combination of monohydrosis with seed-mediated growth in size and shape-controlled synthesis of complex metal oxides nanocrystals as well as the role of nanocrystalline shapes on magnetic properties and the determination of orientation-ordered superstructures formed by shape-controlled nanocrystals of spinel ferrites. First part is concentrated on the shape-control of monodispers spinel cobalt ferrite, CoFe2O4 nanocrystals, which shows a highly reversible shape evolution between a nearly spherical shape and an almost perfect cube. Moreover, the magnetic studies on such cubic CoFe2O4 nanocrystals indicate that the blocking temperature, saturation and remnant magnetization of nanocrystals are solely determined by the volumes (sizes) of nanocrystals. However, the shape of the nanocrystals is a dominating factor for the coercivity of nanocrystals. In second part, magnetite, Fe3O4 nanocrystals with truncated tetrahedral platelets (TTP), tetrahedral platelets (TP), truncated octahedral (TO) and octahedral (OT) shapes have been involved in seed-mediated growth process. Transmission electron microscopy (TEM) analysis indicates that the nanocrystals in each shape tend to selectively accumulate together to form orientation-ordered superlattice structures. The TEM images of the Fe3O4 nanocrystals in shapes of TTP, TO and OT show hexagonal, primitive cubic, and distorted body center cubic (bcc) superlattice structures, respectively. Such magnetic nanocrystals with distinct shapes and their highly orientation-ordered self-assemblies make nanocrystals possess tremendous potentials in fundamental understanding of magnetism and in technological applications of magnetic nanocrystals for high-density information storage.
expected to be directly exposed to vacuum or air at high temperatures. Here, we report the thermal stability of Cu-capped SiO2 membranes formed by mercaptosilane [MPTMS: (HS-(CH2)3-Si-(OCH3)3)] and the effect of vacuum annealing on the interfacial adhesion determined by 4-point bend tests. Cu/MPTMS/SiO2 structures annealed to 700 °C show factor-of-9 higher interfacial energies than Cu/MPTMS/SiO2/MPTMS/SiO2 samples heated to the same temperature. X-ray photoelectron spectroscopy (XPS) of fracture surfaces reveal that enhanced a) interaction between Cu and Si groups and b) siloxane bond formation. Cu/MPTMS/SiO2/MPTMS/SiO2 samples heat treated at temperatures <400 °C, the concentration of siloxane bonds between the MPTMS and SiO2 is low, leading to low debonding values. This is consistent with a high Si 2p/2p intensity ratio of 4.5, obtained by XPS on the Cu fracture surface. At higher temperatures, the ratio drops to 1 indicating fracture at SiO2-MPTMS interface. Our results indicate that Cu-capped SAM layers may meet the thermal stability requirements for incorporating low interfacial adhesion enhanced mechanisms. At temperatures <400 °C, the silicon oxide and the underlying substrates remain undamaged.


GG10.35

Mesoporous silica particles are expected to be useful for catalysis supports and adsorbents because of their mesoporosity. On the other hand, the density and refractive indices of bulk materials can be controlled by involving mesoporous silica particles because air can be introduced with these particles. Also, transparency of bulk materials can be kept when mesoporous silica particles are finely ground in order not to scatter visible light and uniformly dispersed into bulk materials. In this presentation, mesoporous silica nanoparticles synthesized by our company were characterized and applied for low refractive index materials. Our mesoporous silica nanoparticles have ca.30nm in particle size, ca.2nm in pore diameter, 1000m2/g of specific surface area. The refractive index of the particles was estimated to be 1.27. We applied the mesoporous silica nanoparticles to form single layered anti-reflection films. The refractive index of the films containing the mesoporous silica particles became lower reverse-proportionally with the amount of the particles in films. Hence it was confirmed that the mesopores in particles worked effectively to control the refractive index of the films. Also the surface of these mesoporous silica nanoparticles was modified with bulky organic groups to stopper the pores in the particles. These modified particles were solenized or bonded into layers. Films were formed with dispersed modified mesoporous silica nanoparticles and binders. These films showed characteristic values available to a single layered anti-reflection film (the transfer ratio of total visible light = 94%, the lowest reflection ratio = 0.5%).

GG10.36

The response to external hydrostatic pressure of self-assembled multilayer films of gold nanoparticles was investigated in an effort to develop a sensitive, non-intrusive technique to measure hydrostatic pressure at surfaces, similar in function to pressure-sensitive paint, but functional in underwater environments. Gold nanoparticles were initially deposited on thiolated substrates, and alternating layers of hexadecanethiol or decanethiol "spacer" molecules and gold particles were sequentially deposited to create self-assembled films up to ten layers thick. A broadening and red shift in the plasmon resonance band was observed as the interaction distance between the particles was changed on compression. Hydrostatic pressures in the range of hundreds of psi could be measured in this fashion.

GG10.37
Gate Modulation Induced by Field Effects Using Self-Assembled Monolayer-Based Structures at Room Temperature. Dong-un Jin, Christos G. Tjokoudis, Jie Zhang.

This study demonstrates that the ionization at the end groups of Self Assembled Monolayers (SAMs) due to the application of an electric
field results in gate modulation. The observed gate modulation is achieved using bottom gate type three-layered devices, without a semiconductor layer. Electroless plated copper has been used for the bottom gate to realize high adsorption and orientation of SAMs in order to mitigate the occurrence of high leakage currents. Copper ions (Cu^2+) generated during the electroless plating process appear to act as thiol groups in the effect devices to fabricate molecular devices using scanning tunneling microscopy or atomic force microscopy, the field effect devices in this work have been fabricated using simple methods. Also, these devices were operated with large effective contact areas (2 mm^2) between the SAMs and metal electrodes at room temperature. The results of this study suggest that molecular devices designed with large contact areas and fabricated by simple electroless plating processes could provide a new device platform for several future applications.

**GG10.38**

**Ordered Nanostructures for Organic Photovoltaic Cells.**

Vignesh Gowrishankar and Michael McGee, Materials Science, Stanford University, Stanford, California.

The most common strategy for making organic photovoltaic cells efficient is to use a bulk heterojunction in which excitons are split at an interface between two semiconductors with offset energy levels. Since excitons only diffuse 4-20 nanometers in most organic semiconductors before they decay, the semiconductors must be patterned at this length scale. An ideal bulk heterojunction consists of a 100 to 300-nm thick film of one semiconductor with arrays of 10-50-nm wide pores filled with another semiconductor. We will show that the arrays of pores can be made in thin films of silicon or tin using Nanoscale Lithography and Block Copolymer Lithography along with reactive ion etching. The pores can be filled with conjugated polymers by melt infiltration or electropolymerization. The charge carrier mobility of the polymer inside the pores is almost one hundred times higher than that of normal films of just the polymer because the chains align along the straight pore walls. Photoluminescence quenching experiments show that excitons formed in the polymer are split by electron transfer at the organic-inorganic interface.

**GG10.39**

**Effect of Restructuring, Metal Loading and Catalysis Reaction on Nanoporous Carbon.**

Ponnaiyan Ayyappan and Henry C. Foley, Chemical engineering, Penn State University, University Park, Pennsylvania.

The synthesis of nanocarbon materials is typically done with high energy processes including the use of high powered arcs and lasers for graphite vaporization. Recently, progress has been made in the catalytic synthesis of single and multiwalled nanotubes using gaseous precursors and transition metal nanoparticles to produce CNTs. Temperatures in such reactions are still high and control of the product in terms of selectivity is low. These factors motivate the exploration of new approaches the synthesis of carbon nanostructures with nanoporous carbon as the metal addition. We also like to emphasize the effect of sialsi and transition metals addition and gas phase catalytic reaction on the nanoporous carbon.

**GG10.40**

**Possible Superconductivity in Langmuir-Blodgett Films Based on Diallyldimethylammonium-Au(dmit)2 salts.**

Yoshio F. Miura, Shin-ichi Morita, Ryo Watanabe, Michio Sugii, Masato Hedo and Yoshida Uwotoku, Department of Functional Chemistry, Toh University of Yokohama, Yokohama, Kanagawa Prefecture, Japan; Institute for Solid State Physics, University of Tokyo, Kawasaki, Chiba Prefecture, Japan.

Fabrication of a superconducting Langmuir-Blodgett (LB) film is one of the long-standing goals among various trials for fabricating LB films with electronic and opto-electronic functions. Since the LB technique allows us to transfer two-dimensional (2D) molecular sheets from the air/water interface onto solid supports and fabricate tailored mono- and multi-layered systems, the realization of superconductivity will open up the possibility for a variety of applications in the future. We have already reported that the LB film of ditetradecyldimethylammonium-Au(dmit)2 salts shows an in-plane conductivity temperature dependence in the range 230-300 K [1] and that the ac magnetic susceptibility suggests the existence of the Meissner state below 4 K [2]. However, the resistance drop upon cooling is not seen for the sample batches of majority in the measurement down to 1.2 K [3]. In this paper, we report that the hydrostatic pressure induces the resistance decrease on cooling as for the 2C<sub>14</sub>-Au(dmit)<sub>2</sub> LB films. The 2C<sub>14</sub>-Au(dmit)<sub>2</sub> LB films was synthesized following the procedure of Stimecke et al. /4 [4] and spread at the air/water interface using a 1:1 mixture of acetonitrile and benzene. The horizontal lifting method was utilized and the 2C<sub>14</sub>-Au(dmit)<sub>2</sub> LB film at the air/water interface was transferred onto a 0.1-mm-thick poly(ethylene terephthalate) (PET) sheet. The as-deposited LB film was rendered by an electrochemical oxidation [5] and the resistance was measured along the film plane by an ac four-probe method in the temperature range 0.5-290 K. A hydrcarbond oil (Diaphne Oil 7373, Idemitsu, Co. Ltd) was used as the pressure medium. The resistance of the 2C<sub>14</sub>-Au(dmit)<sub>2</sub> LB film decreases with increasing pressure, reaching a 0.6- times smaller value at 0.7 GPa. Then the pressure cell was clamped at 0.7 GPa and was cooled down to 0.4 K. A different sample cut from the same batch was also set outside the pressure cell and the ambient resistance was measured as the reference.

**GG10.41**

**Signatures of Quantum Transport in Self-Assembled Epitaxial Nickel Silicide Nanowires.**

Toshiko Kim, J. F. Lin, Zhan He, Jon P. Bird, David J. Smith, and Peter Bennett, Physics, Arizona State University, Tempe, Arizona; Electrical Engineering, Arizona State University, Tempe, Arizona, Science and Engineering of Materials Program, Arizona State University, Tempe, Arizona; Center for Solid State Science, Arizona State University, Tempe, Arizona.

We have measured the electrical properties of self-assembled epitaxial NiSi2 nanowires (NWs) formed from deposition of one monolayer Ni on stepped Si(111) in UHV at 500 C. This forms NWs with single-orientation and average dimensions 15 nm wide by 1.5 microns long. Samples are removed from UHV and leads are connected using electron-beam lithography with PMMA and metal lift-off. The transport measurements show quantum corrections due to weak localization and electron-electron interactions. Analysis of the magneto-resistance indicates that electron phase coherence in the NWs is limited by Nyquist dephasing below 10 K, and by electron-phonon scattering at higher temperatures. The breaking of spin-orbit scattering lengths is found to be 45 nm and 3 to 7 nm, at 4.2 K, respectively, similar to values for thin epitaxial NiSi2 films.

**GG10.42**

**Investigation of the Contact Formation Between Macro-Molecular Building Blocks and Mesoscopic Electrode Materials.**

Nielas Dan, Brian Doran, Chris Braunagel, Martin M. Beerbom and Rudy Schaf, Electrical Engineering, University of South Florida, Tampa, Florida.

The contact formation between macro-molecular building blocks (nano-particles, nanotubes, oligonucleotides, peptides etc.) and mesoscopic electrode materials (metals, semiconductors, dielectric materials) is currently not very well understood. This is for example indicated by the considerable range of recent experimental results we have reported to deoxyribonucleic acid (DNA) nanoscale, which have been found to be insulating, semiconducting and metallic. It is likely that the various methods and materials used to connect to single DNA strands led to a variety of contact types and in fact from tunneling barriers, to Schottky or Ohmic type. In this context, we have developed a measurement methodology to gain detailed insight into the electronic structure of macro-molecular, and to better understand the mechanisms that effectively prevent in-vacuum evaporation. The enabling technique used in our experiments is electrospray (ES) thin film deposition, which allows us to prepare macro-molecular thin films in vacuum without significant contamination. Here we present first results of this technique for ribonucleic acid (RNA)/metal interfaces, which serve as a model...
system for DNA interfaces. In our experiments, we have successfully been able to deposit DNA polymers directly from solution in an UV environment. This method is very promising for large volume mass production. The deposited nucleic acids were observed to form a gelatinous layer on the substrate. The formation of ordered binary assemblies. As model systems, we used the mixtures of differently sized Fe2O3, CoPt3 - Fe2O3, PtSe - Fe2O3, CdSe - CdS nanocrystals. For all these combinations, ordered AB2 and AB3 binary assemblies have been successfully and reproducibly formed. Perfectly faceted macroscopic (20 - 100 microns) colloidal crystals of CoPt3, PtFe, Fe2O3 and CdS nanocrystals have been grown. HRSEM investigation showed the long range ordering of the nanocrystals with the coherence over entire colloidal crystal. Colloidal CdSe nanocrystals and CdS/CdSe heterostructures were self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanocrystals can form nematic, smectic and crystalline phases with ordering in both lateral and longitudinal directions. Self-assembled CdSe/CdS nanorods can form spherical textures with characteristic birefringence in a light microscope. CdSe/CdS nanorod heterostructures were self-assembled into highly luminescent superlattices with low re-absorption effects.

SESSION GG11: Structure and Intrinsic Properties ofNanoassemblies II
Chairs: Paul Braun and Alexander Wei
Thursday Morning, December 2, 2004
Room 311 (Hynes)

8:30 AM *GG11.1
Intrinsic Properties of Nanocrystal Self-Assembled.
Marie-Paule Pileni, Laboratoire LM2N, University P et M Curie, Paris, France.

Various self-organization of nanocrystals will be presented with formation of 2D compact hexagonal network, 3D colloidal crystals in FCC structure, ring, dots, lines, tubes and labyrinths. The collective properties induced by the self-organization are mainly due to dipolar interactions. However intrinsic collective properties are also observed. As example vibrational coherence is discovered in 3D FCC supracrystals. If the evaporation rate of the solvent is slower than the evaporation rate of the nanocrystal solution, evaporation is made evident in low-frequency Raman scattering by the narrowing of the peak due to the quadrupolar modes of the nanocrystals. However, as predicted by theory, this narrowing is not visible when the sizes of the supracrystals become comparable or larger than the light wavelength. Furthermore, the supracrystallization is manifested by the shift to low frequency of the Raman peak due to the Lorentz effective field created by the light induced plasmon-polarization of the nanocrystal supracrystal. An interesting example of supra crystal formation is crystallization process occurring at low temperature whereas it is usually observed at high temperature. This opens a new area in the crystal growth domain. Finally we demonstrate that the nanocrystals are used as mask for lithography techniques.

9:00 AM *GG11.2
Ordered and Non-Ordered Heterocoagulation of Ultrafine Particle Systems. Gary R. Maskal1,2, W. Craig Carter1 and Yet-Ming Chiang1.

1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York.

The heterocoagulation of colloidal particles is a widely studied topic and the subject of an extensive body of literature. In recent work, we have found certain regimes where the suspension behavior cannot be explained by existing heterocoagulation theory. At low ionic strengths and/or small particle sizes, charge balance effects can cause the heterogeneous size such that the solution is stable for long times despite a similar number of positively and negatively charged particles. A shift in behavior from a stable suspension to a colloidal gel to a dense colloidal glass is observed as the electronegativity of the system are altered. This anomalous heterocoagulation behavior is of special interest for the formation of ionic colloidal crystals, where a dense colloidal heterocoagulated liquid is necessary to allow the nucleation and growth of complex ordered ionic structures. We present an electrostatic model that can explain this behavior. The nucleation behavior of ionic colloidal crystals from dense colloidal liquid is also studied via Monte Carlo simulations allowing the calculation of the nucleation barrier.

9:15 AM *GG11.3
Ordered Binary Structures and Self-Assembly of Shape Controlled Nanocrystals. Elena Shevchenko1,2, Dmitri V. Talapin2, Stephen O'Brien1 and Christopher Murray2.


The monodisperse nanocrystals can self-assemble into one-, two- and three-dimensional superstructures. Various magnetic (CoP3, FePt, Fe2O3, CoPd) and semiconductor (CdS, PbSe) nanocrystals were used as building blocks for the formation of 2D and 3D ordered superstructures. Systematic investigation was performed to reveal the conditions favouring formation of ordered binary superlattices. We have investigated the effect of various stabilizing agents, solvents, temperature, size ratio and nanoparticle concentration on the formation of binary assemblies. As model systems, we used the mixtures of differently sized Fe2O3, CoPt3 - Fe2O3, PtSe - Fe2O3, CdSe - CdS nanocrystals. For all these combinations, ordered AB2 and AB3 binary assemblies have been successfully and reproducibly formed. Perfectly faceted macroscopic (20 - 100 microns) colloidal crystals of CoPt3, PtFe, Fe2O3 and CdS nanocrystals have been grown. HRSEM investigation showed the long range ordering of the nanocrystals with the coherence over entire colloidal crystal. Colloidal CdSe nanocrystals and CdS/CdSe heterostructures were self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanocrystals can form nematic, smectic and crystalline phases with ordering in both lateral and longitudinal directions. Self-assembled CdSe/CdS nanorods can form spherical textures with characteristic birefringence in a light microscope. CdSe/CdS nanorod heterostructures were self-assembled into highly luminescent superlattices with low re-absorption effects.

SESSION GG12: Novel Responses and Applications ofNanoassemblies I
Chairs: Albert Schoening and Humberto Terrones
Thursday Morning, December 2, 2004
Room 311 (Hynes)

10:30 AM *GG12.1
Self-Assembly and Magnetic Switching of Cobalt Nanoparticle Rings. Alexander Wei1, Steven L. Tripp2 and Rafał E. Dunin-Borkowski.

1Chemistry, Purdue University, West Lafayette, Indiana; 2Materials Science, University of Cambridge, Cambridge, United Kingdom.

Dispersions of single-domain Co nanoparticles are capable of assembling into bracelet-like nanorings as a result of magnetic dipolar interactions. Investigations by TEM demonstrate that the self-assembled nanorings are kinetically stable, and that their mechanism of self-assembly is distinct from hole nucleation and other deposition effects mediated by solvent evaporation. Off-axis electron holography reveals that nanoparticles collectively form chiral flux closure (FC) domains when assembled into rings. Such binary states are stable at room temperature, and have intriguing potential as nonvolatile memory elements. We have recently determined that the polarity of the FC states can be switched reliably by out-of-plane magnetic fields; mechanisms for this magnetization reversal will be discussed.

11:00 AM *GG12.2
From Nanoscale Building Blocks to Macroscopic Devices. Yunfeng Lu, Donghai Wang, Byron McCaughhey, Rong Kou, Maria P. Gill and Xuan Li.

Chemical & Biomolecular Engineering, Tuohai University, New Orleans, Louisiana.

Nanoscale materials often show unique and superior physical, chemical, and tribological properties. The promise of nanotechnology is fulfilled when these unique properties are translated into dimensions that devices can use. A significant step towards this goal is the hierarchical assembly of nanoscale building blocks into controlled macroscopic structures. Self-assembly, an approach that...
utilizes non-covalent interactions to organize building blocks into higher order structures, has emerged as a most promising approach. This presentation will address the design, synthesis and applications of self-assembled nanoscalestructured materials through static and responsive self-assembly. For example, we utilized self-assembled mesoporous silica as templates and electrodeposition to synthesize 2D and 3D nanowires. These robust nanowire thin films show promising applications in fuel cells, thermoelectric, hydrogen separation, high surface area electrodes, magnetic materials, photovoltaics, sensors, and other applications. This presentation will also discuss the concept of nanowire thin films of the nanowire spanning the electrodes defines the active region, oxide can be a sensor, ferroelectric, dielectric, semiconductor, or interconnects integrated within the building block. The functional oxide that a band gap engineered funnel for excitation energy can be built utilizing molecular units, offers an excellent tool to construct cheaply and easily nanoelectronic devices, where nanoscale building blocks, such as MOM nanowires, and the assembly of the nanowires can be used as templates to produce thin films of metals with a thinner films for equivalent electrodeposition times, and so somewhat smaller surf a ce area enhancements. However, the demonstration that specifically nickel foam such as is used in nickel/cadmium batteries, fuel cells, sensors and supercapacitors. Work carried out by the groups of Attard and Bartlett showed that non-ionic surfactants can be used as templates to produce thin films of metals with a regular hexagonal pore arrangement. Such thin films have surface areas which are much higher than that of the original electrodes. We have recently demonstrated that non-ionic block copolymers consisting of poly(oxyethylene) and poly(propyleneoxide) blocks can also be used as templates from which thin metal films with a regular arrangement of pores can be electrodeposited. Using Pluronic P123 as template a hexagonal array of pores with a pore to pore spacing of 7.5 nm is produced from both nickel and cobalt salts. The conductivity of the block copolymer solutions appears to be somewhat lower than that for the non-ionic surfactants leading to thinner films for equivalent electrodeposition times, and so somewhat smaller surf a ce area enhancements. However, the demonstration that block copolymers can also be used as soft templates for such systems holds the promise of a wider range of structures and length scales than is available with surfactants. We have also extended the application of such materials to three dimensional substrates, specifically nickel foam such as is used in nickel/cadmium and nickel/metal hydride batteries. For such systems we see a large surface area enhancement after formation of a mesoporous nickel film. Preliminary evidence indicates that the mesoporous film is formed throughout the nickel foam.

11:45 AM **GG12.4**


There has been growing interest in the "bottom up" approach to building nanoelectronic devices, where nanoscale building blocks, such as nanowires (metals, semiconductors, oxides), are fabricated in isolation and assembled into nanocircuits. The "bottom up" approach offers several key advantages over the conventional "top down" microelectronics approach, including higher circuit densities and processing compatibility. Current nanoelectronics technology uses nanowires that are assembled across photo-lithographically deposited metal-contact-pad electrodes to create devices. In this case, the length of the nanowire spanning the electrodes defines the active region, which is very difficult to control precisely. In order to address this critical issue, we propose the concept of the engineered metal-oxide-metal-MOM nanowire, in which a MOM nanowire (50 to 100 nm diameter; Au or Pt) with a small segment (50-100 nm length) being replaced by a functional oxide. In other words, a MOM nanowire has a functional oxide of precise dimensions with metal interconnects integrated within the building block. The functional oxide can be a sensor, ferroelectric, dielectric, semiconductor, or magnetic material. Thus, the MOM nanowires have the potential to take the field of "bottom up" nanoelectronics to the next level of sophistication. In addition to this approach, we have developed two different methods of electrochemical deposition within porous templates to synthesize such MOM nanowires. Both methods are generic, and they can be used to fabricate a wide variety of MOM nanowires. Here we have synthesized two specific examples of MOM nanowires: Au-BaTiO3-Au (ferroelectric) and Au-BaTiO3-Au (ferroelectric). Synthesis methods, characterization results from the MOM nanowires, and the assembly of the nanowires into functional nanodevices will be presented.

**SESSION GG13: Novel Responses and Applications of Meso-assemblies II**

**1:30 PM **GG13.1

**Self-Assembled P-Conjugated Systems**, Albert Schenning; Eindhoven University of Technology, Eindhoven, Netherlands.

Supramolecular chemistry, which makes use of self-assembling molecular units, offers an excellent tool to construct cheaply and easily nanoelectronic components in a "bottom up" fashion. In particular, the nanometer scale self-assembled oligomers are used as building blocks in these nanosized components one can expect new, unprecedented electrooptical properties. During my presentation, examples will be given on how p-conjugated systems can be self-assembled and applied in supramolecular electronics.

**2:00 PM **GG13.2


The successful application of quantum dots in many device concepts requires the ability to control interparticle separation. As a result, several strategies have been developed in the literature in an effort to address this challenge. Two popular examples include the use of complementary DNA strands to mediate reversible aggregation in solution and the control of interparticle interactions through the engineering of shell thickness. [1,2] Despite the diversity of approaches available, they generally have a synthetic feature in common: The need for an iterative approach to controlled interparticle separation. Using gold nanoparticles, we demonstrate a method that affords dynamic control of interparticle interactions within a single material. Our approach relies on generating composite core/shell particles comprised of a gold core, and of a shell of thermosensitive polymer poly(N-isopropylacrylamide) (pNIPAAm) to provide stimulus responsive control of interparticle coupling within particle arrays. Reversible changes in particle size were successfully translated into reversible changes in optical properties of a film consisting of self-assembled composite core/shell particles. Variable UV-vis spectroscopy suggests that the thermally induced change in interparticle separation occurs coherently throughout the film. [1] J. J. Storhoff, A. A. Lazurides, R. C. Mucic, C. A. Mirkin, R. L. Letsinger, G. C. Schatz, J. Am. Chem. Soc. 2000, 122, 4640 2; C. B. Murray, C. R. Kagan, M. G. Bawendi, Science 1995, 270, 1305. **We thank Peter Codella and Hans Grade for assistance in characterization.

**2:15 PM **GG13.3

**Exciton Recycling in Graded Gap Nanocrystal Structures**, Thomas Frey1, Thomas A. Klar, Stefan Schietinger, Andrey L. Rogach and Joachim Feldmann; Physics Department, LMI Munche, Photonics and Optoelectronics Group, Munich, Germany.

Motivated by natural antenna complexes and by semiconductor heterostructure lasers, we consider a cascaded energy transfer (CET) structure made of CdTe nanocrystals (NCs). Funnel like band gap profiles are realized applying layer-by-layer assembly to CdTe nanocrystals of distinct sizes. For high-energy excitation, the CET structure with only one layer of red-emitting NCs emits 4 times more red light than a reference sample of equal absorbance consisting of seven layers of red emitting NCs. The super-efficient exciton funneling can be explained by a recycling of surface trapped excitons that are usually lost for photoluminescence [1]. The energy of the excitonic transition in CdTe nanocrystals can easily be tuned over the whole visible spectral range by changing their size. NCs can also be used as building blocks for mesoscale architectures, often called artificial solids. One example is a set of adjacent layers of differently sized CdTe NCs that shows high energy transfer rates [2]. We demonstrate that a band gap engineered funnel for excitation energy can be built using layer-by-layer (LbL) assembly of CdTe NCs. Directed energy transfer between layers of differently sized NCs allows the excitation energy into the active zone, i.e. into a single layer of the largest NCs placed in the center of the funnel. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra show two important features. First, there is negligible emission from the NCs. The small particles apparently serve as donors and the excitation energy is efficiently transferred along the gradient towards the layer of the largest particles. Second there is a clear enhancement of the emission intensity of the largest NCs. The GE structure with a single emitting layer shows a 4 fold increased quantum efficiency compared to a reference sample containing 7 layers of the largest NCs. Hence the final exciton density in the single emitting layer of large

Dynamic control over the interaction of liquids with a solid substrate is of great interest in many research areas ranging from biology and chemistry to physics and nanotechnology. Only recently, studies have been expanded to include dynamic control over the interaction of liquids with nanostructured surfaces. In this work, the properties of recently demonstrated electrically tunable nanostructured superhydrophobic surfaces are further investigated. The dependence of the superhydrophobic wetting transition on the topography of the nanostructured layer, its electrical properties, and its surface coating are investigated. The reversibility of this transition and its dependence on the geometry of the nano-size features are discussed. The reported results provide novel methods of manipulating liquids at macro-scale. A wide range of applications, including micro- and nanofluidics, chemical microreactors, sensors, integrated thermal management in microelectronics, and optics communications may benefit substantially from the ability to dynamically tune the liquid-solid interactions.

3:30 PM *GG13.5 Nanostructured Materials Switched by Double-Layer Charge Injection and Retained in Vacuum. Dong-Seok Sub1, Alan G. MacDiamid1, Edgar Munoz2, W. Joshua Kennedy2, Zee V. Vardeny3, Anwar A. Zakhidov4, Vladimir Agranovitch4, Alan B. Dalton1, Steve Collins1, Mei Zhang1, Von H. Ebron1, John F. Ferrara1, Ali Aliev5, S. Lee4 and Ray H. Baughman4; 1Department of Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, Texas; 2Department of Physics, University of Utah, Salt Lake City, Utah. We discovered a surprising generic method for charge-injection-based tuning of the bulk properties of electrolyte-free nanostructured materials over a wide range without incurring dopant intercalation and associated problematic structural changes. Specifically, we found that carbon nanotube sheets, nanoporous metals, and other nanostructured materials, retain injected charge and associated structure and properties changes when non-faradaically injected with charge in a liquid-electrolyte supercapacitor and then removed from the electrolyte and dried in vacuum. Charge injection for carbon nanotube sheets in an electrochemical cell causes a quasi-parabolic order-of-magnitude increase in electrical conductivity, much of which is retained when the electrolyte is either evaporated or frozen. The implications of these discoveries are explored for diverse devices that function without electrolyte contact with electrochemically switched elements.

4:00 PM GG13.6 Efficient and Reliable Fabrication of CNT Point Electron Sources by Dielectrophoresis. Jian Zhang1, Jie Tang2,1, Guang Yang1, Qi Qiu1, Lu-Chang Qin2,4 and Otto Zhou1,2; 1Physics and Astronomy, UNC-CH, Chapel Hill, North Carolina; 2National Institute for Material Science, Tsukuba, Japan; 3Xintek Inc., Chapel Hill, North Carolina; 4Curriculum in Applied and Materials Sciences, UNC-CH, Chapel Hill, North Carolina. Although carbon nanotubes (CNTs) have shown great promise for enabling nano-scale electronic devices, efficient and reliable methods for assembly and integration of CNT are still currently lacking. Here we report the fabrication and electron field emission properties of short CNT tips by dielectrophoresis. Aligned CNT tips comprising either SWNT bundles or MWNTs were assembled on sharp metal wires with controlled length, diameter and orientation. Over 90% of the tips were confined within a 90° degree angle from the cone axis of the metal wire. Due to the interfacial morphology they adhere strongly to the metal supports, which ensure the stability under high electrical fields, and results in mechanical vibration. The CNTs are capable of delivering high and stable electron field emission currents of 3-5 μA (10A/cm² in density). The emitters thus fabricated can potentially be used as the field emission electron sources for precision vacuum electronic instruments such as electron microscopes.

References: J. Tang, et al., Adv. Mater., 2003. 15(15): p. 1352. J. Zhang, et al., Adv. Mater., in press 4:15 PM GG13.7 Fabrication and Characterization of Carbon Nanotube-Based AMP Probes by Dielectrophoresis. Jie Tang1,2, Guang Yang1, Qi Zhang2, Ben Maynor3, Jie Liu3, Lu-Chang Qin2,4 and Otto Zhou1,2; 1National Institute for Materials Science, Tsukuba, Ibaraki, Japan; 2University of North Carolina, Chapel Hill, North Carolina; 3Duke University, Durham, North Carolina. Dielectrophoresis is often used to manipulate and assemble colloidal particles, and has recently been applied to carbon nanotubes (CNTs) [1]. We here present a reliable and high throughput dielectrophoresis method for fabrication of CNT-based atomic force microscope (AFM) tips at room temperature. An alternating-current (AC) electrical field was used to align and assemble the CNTs dispersed in a liquid onto the apex of a commercial AFM probe. The tip length and orientation are controlled and predetermined. They are typically 0.5 to 10 mm in length and 20 - 80 nm in diameter. Their ability to image structures with high aspect ratios will also be demonstrated. Morphological characterization using scanning electron microscope (SEM) and transmission electron microscopy (TEM) will also be presented. The dielectrophoresis method can also be extended to the fabrication of AFM and STM probes using other nanostructured materials. [1] J. Tang, B. Gao, H.Z. Gong, O.D. Velev, L.C. Qin, and O. Zhou, Adv. Mater. 15, 1352 (2003).

4:30 PM GG13.8 Novel Approach to the 3-D Fabrication and MicroSynthesis of Functional Molecularly Imprinted Polymer (MIP) Using Microstereolithography and Microbulldrop Reactors. Kyung M. Chai1,2, John A. Rogers1,2 and Kenneth J. Shea1,2; 1Chemistry, University of California-Irvine, Irvine, California; 2Materials Science and Engineering, University of Illinois at UC, Urbana, Illinois; "Bell Labs, Lucent Technologies, Murray Hill, New Jersey. Microfabrication technology offers us rapid assembly and integration of unconventional devices since small features fabricated on a variety of substrates have produced numerous active devices, which satisfy a set of our demands in miniaturization. Especially in the development of advanced plastic/organic/molecular electronics, this technology allows us to produce economic devices with high performance using 'soft' organic/polymeric materials. Organic photoresists such as SU-8 have been widely used for pattern fabrication. Recently, there is a growing interest in the pattern integration using functional materials. In this work, we present a novel approach to the 3-D microfabrication and microsynthesis of unconventional functional materials to expand current technology to advanced levels for our diverse demands. Here, we have introduced a molecularly imprinted polymer (MIP) as a promising candidate of advanced patterns with specific functions. MIP is a highly cross-linked macroporous thermoset with both high internal surface areas and specific molecular recognition binding sites, which may be useful for chemical or bio-sensor applications. Using the MIPs' system attached with fluorescent template molecules, we fabricated a 3-D molecular architecture in the (600 μmx600 μmx100um)-geometry through 'microstereolithography'. We also generated a fluorescent MIP pattern in 100 um line-width by 'micromolding technique' in capillaries using PDMS microchannel photoresists. In this work, we also introduced a novel approach to synthesize nano- or micro-sized MIPs polymer particles using a 'microfluidic droplet reactors'. As the MIPs' particle size was decreased, we obtained MIPs particles with higher affinity. This is a new method to produce 'monoclonal MIPs particles', which have only high affinity binding sites with specific molecular recognition function.