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

November 29 - December 2, 2004

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* Invited paper

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Adding a New Dimension in Nanoscale Materials: Metal Nanoparticles with Phase Separated Ligand Shells.

Francesco Stellacci, Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts.

Ligand coated metal nanoparticles are promising nanosize materials 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. This unique sub-nano-structuring of their ligand shell provides new opportunities to deposit these peptide nanostructures on surfaces. Indeed, by systematically varying 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 6 Å wide on the ligand shell of nanoparticles. The formation of both 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 mechanism that leads to the formation of this supramolecular ordering will be discussed. These particles show unique and unexpected solubility, self-assembly and surface chemistry properties, in particular they show a remarkable resistance to protein nonspecific adsorption.


Directed Assembly of Metal-Organic Nanoarchitectures.

Klaus Kern, 1Nanoscale Science Department, Max Planck Institute for Solid State Research, Stuttgart, Germany; 2École Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The engineering of nanostructures from molecular building blocks provides the unique advantage that organization and functionality can be manipulated by chemical design. With the thoughtful choice of the molecular architecture and interaction motifs, highly organised supramolecular architectures can be realized providing tailor-made properties. In addition, molecular nanostructures offer a natural interface to the biological world and can be employed to explore the coupling of inorganic structures to living organisms or cells and to implement biological principles in devices and sensors.

In this talk I demonstrate the use of specific metal ligand interactions for the construction of hybrid nanoarchitectures. The first example addresses the use of large biomolecules like the tobacco mosaic virus (TMV) for noncontacting fabrication techniques. The well-defined chemical groups at specific locations of the coat proteins of the virus can act as ligands for metal ions. We use this chemical functionality for the selective growth of metal nanowires and/or coatings from metal ion solutions. The second example discusses the construction of complex metal-organic nanoarchitectures at surfaces using concepts from coordination chemistry. Well-ordered supramolecular structures and coordination networks with specific topological and high structural stability are fabricated by self-assembly of functional organic molecules and for example on single crystal substrates.

Uniform mesoporous silica films with arrays of oriented cylindrical pores.

Sivakumar Nagarajan, Mingqi Li, Rajaram A. Pai, 2C. Weinmann, 2Christopher K. Ober, 2Thomas P. Russell, 2and James J. Watkins, 2Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, Massachusetts; 3Material science and engineering, Cornell University, Ithaca, New York.

Ordered mesoporous metal oxide films are of enormous interest for applications in catalysis, separations, photonics, electronics, sensing and detection devices. One unresolved challenge has been the fabrication of robust films with cylindrical pores aligned perpendicular to the plane of the substrate. Such an arrangement renders the pore structure accessible for the intended application. We have developed a novel approach to mesoporous films in which metal oxide precursors are rapidly diffused through and selectively condensed within one domain of a preorganized block copolymer film that is dilated with supercritical carbon dioxide. Using this two-step approach, the structural details of the block copolymer template are transferred to the metal oxide network with high fidelity. Thus structures imparted wholly in the block copolymer during template formation carry over into the mesoporous silica enabling prescriptive control of film structure by template manipulations. Recently, the rapid preparation of micro phase-separated block copolymer films with cylindrical domains oriented normal to the substrate surface using controlled solvent evaporation has been described. Here, we report the replication of these oriented templates to yield uniform mesoporous hollow spheres while permitting the passage of smaller molecules will be described.

SESSION GG1: Nanotemplating for Meso-scale Assembly I

Chairs: Yunfeng Lu and G. Ramanath
Monday Morning, November 29, 2004
Room 311 (Hynes)

8:30 AM *GG1.1
Dip-pen Patterning of Peptide Amphiphile Nanofibers. Samuel I. Stupp1,2,3 and Hongzhou Jiang1, 1Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2Chemistry, Northwestern University, Evanston, Illinois; 3Feinberg School of Medicine, Northwestern University, Evanston, Illinois.

Self-assembly of peptide amphiphile (PA) molecules into one-dimensional cylindrical nanostructures has been studied recently in our laboratory. These nanostructures measure a few nanometers in diameter and microns in length, and their peptide segments are presented on the nanofiber surface. Combined with patterning approaches such as dip-pen nanolithography (DPN), evaporated dip-pen self-assembly of these PA nanofibers offers interesting opportunities to deposit these peptide nanostructures on surfaces. We report here the surface-driven self-assembly of PA molecules using direct patterning techniques to create reproducibly aligned PA nanofiber patterns on silicon substrates. We also demonstrate that these nanofibers can retain their alignment when another set of nanofibers of different orientation is created on the first pattern. By tuning patterning conditions, we also demonstrate the possibility of depositing on surfaces highly aligned close-packed arrays of nanofibers.

9:15 AM *GG1.3

500 nm diameter hollow spheres containing a periodic array of 3 nm pores in a hexagonal lattice in the shell wall were created through liquid crystal templating of the growth of ZnS on colloidal particles, followed by dissolution of the colloidal particle. The colloidal particles were first dispersed into a lyotropic liquid crystal formed from a mononic surfactant and water that also contained thioacetamide and zinc acetate. Then, ZnS, formed from the reaction of thioacetamide and zinc acetate, heterogeneously deposited in a superlattice structure as defined by the liquid crystal on the surface of the colloidal particle. The mineralized colloidal particles were separated from the liquid crystal, and the colloidal particles were dissolved, resulting in a hollow sphere perforated with a periodic array of nanoholes. Both silica and polystyrene colloidal particles could be used as templates; silica particles are removed with fluoride ions, while polystyrene particles are removed with organic solvents. Initial experiments which demonstrate the sequestering of macromolecules within the mesoporous hollow spheres while permitting the passage of smaller molecules will be described.

9:30 AM *GG1.4
Fabrication of Asymmetrically Coated Colloid Particles by Microcontact Printing Techniques. Oliver J. Cryne, Dept of chemistry, University of Hull, HULL, United Kingdom.

We developed a novel method for preparation of asymmetrically coated colloid particles by using a microcontact printing technique. First, water-insoluble ionic polystyrene sulfonic acid was deposited on PDMS stamps were printed onto latex particle monolayers of opposite surface charge in order to produce spherical latex particles of dipolar surface 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 electro rheological fluids.
silica films with an array of orientated and accessible cylindrical pores. The process is rapid, efficient and easily extendable to other metal oxides. 1. Pui et al., Science 2004, 303, 507.

Patterning Complex Multi Component Structures with Ferroelectric Nano Lithography, Dawn Bennett, 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 precursors is manipulated to control surface electronic structure and local chemical reactivity. Paradigms for ferroelectric domain patterning using scanning probe microscopy, electron beam lithography and microcontact stamping are presented. Photo reaction of inert and functionalized porphyrins and, peptides, and semiconductor nanoparticles allows assembly into configurations that yield nanodevices, such as optoelectronic switches and modulators. Sequential and simultaneous patterning of multiple compounds will be demonstrated.

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 nanoassemblies 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 morphologies 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.

Solution Stamping Nano-Lithography for Patterned Deposition of Inorganic Films, Nanaine A. Chang, Julia W.P. Hsu, Jacob J. Richardson and Paul G. Chem; Sandia National Laboratories, Albuquerque, New Mexico.

In solution stamping nano-lithography (SSNL), an elastomeric stamp containing relief patterns is first “inked” with a sol gel precursor chemistry or other reaction conditions. After deposition, the stamp is removed, leaving behind an image of the relief pattern on the substrate. If a lattice-matched substrate is used, the patterned thin films may be epitaxially regrown on 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 junction fabrication and top-down patterned self-assembly of nanoparticle films is 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.

Fabrication of 3D Nanoarchitectures by Way of Nanocopying of Natural Substances. Copying of DNA Strand and Artificial Pores, Toyotomi Kunitake,1,2 Shigemori Fujawahra,1, Rue Tsukak2 and Janguo 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 covering of a given template with ultrathin (nanometer-thick) layers and 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 both types 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 creating morphological characteristics of the copied object. Infinite amorphous solids such as organic polymers, inorganic glasses and metals may be candidate materials for this purpose. Certainly 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 material. We applied this method to natural substances. Cellulose fibers possess surface hydroxyl 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 retained except for a little 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) (3) S. Fujikawa, T. Kunitake, Analytical Chemistry, 75(2003), pp. 2839-2843 (2) J. Huang, T. Kunitake, J. Am. Chern. Soc., 125(2003), pp. 11534-11535 (3) R. Takali, S. Fujikawa, T. Kunitake, in preparation.
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 unique nanoscale confinement effect on 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 Mesoassembly
Chairs: Paul Braun, Eric Lu and G. Ramanath
Monday Afternoon, November 29, 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 what needs to be done to pattern the 45 nm features 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 photolithography today) can be extended beyond 55 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 technology and future potential, we will explore a way out of the coming crisis that may lie in the use of some form of nanoimprint technology, which presently still is 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 Meso-Scale Self-Assembly, George M. Whitesides, Logan McCarty, Qiaobing 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 mesoscopic systems by templated self-assembly from nanoscopic 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 complicated structures having electrical, optical, biological and 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 nanoelectronics. 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 patterns nanostructures 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 presses a mold into the molten material. We will show our achievements of sub-10 nm feature sizes in LADI on SiC and metals (Au and Cu), and new applications of LADI in wafer planarizations. Finally, we will present lithographically-induced self-assembly (LISA), where self-assembly of nanostructures are guided by much larger 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 biomacromolecules. 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 monodispersity continues to be an important issue with biological nanoparticle synthesis methods, shape modulations 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. We have developed a very complex structure and present nanoscale reactive scaffold 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 Nanobiotechnology: Concepts, Applications and Perspectives' (ed. C.M. Niemeyer, C.A. Mirkin), C.V. Weltey (VCH, Weinheim, 2004). [2] S. Mandal, S.K. Arumugham, S.D. Adyanthaya, R. Parshara, 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 introduced 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 of the bacterium Escherichia coli. A feature of these strategies is 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 adherence of the bacterium to that surface through expression of the selected surface. Our population was designed to simplify genetic analyses of the recovered polypeptides. We find the interactions of proteins with inorganic materials show many similarities with 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 mediate gold crystal formation and dissolution utilize common enzymatic mechanisms. We imagine the diverse adhesive, structural, reactive and catalytic traits of proteins can provide new insights to nanomaterials.


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-assembling 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 these 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-alkylphosphine oxide (TOP) 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 cysteine derivatives 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 quickly to form cystine. Cystine, 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 conjugating groups 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 complex. Alternatively, genetic modification of the N- and C-termini of self-assembling proteins with suitable nucleophilic peptide chains can facilitate a more selective binding of proteins directly to the QD surface. We present PL data and striking microscopy approaches that afford excellent control over the construction of QD arrays or chains.


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 ballistic 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 development of new routes for that may be orthogonal to top-down processing. Pursuant to these requirements carbon nanotubes and bio-inspired materials are being studied extensively for such device and interconnect applications. Along this line we have investigated genetically engineered polypeptide molecules that exhibit beta-sheet protein folding as a platform from which to synthesize self-assembling conducting networks. These molecules have additional advantages such as monodispersity and synthetic controllability. The polypeptide under investigation consists of an alanine and glycine -(ala-gly)3- backbone. Successive beta-turn groups consist of tyrosine, glutamic acid, histidine, and lysine groups yielding self-bridged beta-turns on one side of the sheet opposite phenol-containing turns. Scanning probe microscopy (SPM) of these polypeptide molecules on different substrates such as nickel and highly ordered pyrolytic graphite (HOPG) has revealed the formation of secondary intra-molecular assembly into a novel fibril structure. Synthetic scaling of the length of the polypeptide molecule leads to a corresponding scaling of the observed fibril width. Comparison with beta-sheet dimensions from molecular modeling permits an unambiguous determination of the beta-sheet orientation within the fibril. Coupled with resonance Raman spectroscopy analysis of the polypeptide material in solution we conclude that the fibril represents an end-to-end planar stacking of the beta-polyptide beta sheets. The effects of changing the parameters influencing pH, concentration and temperature have been studied which has laid the path for further progress in understanding the nature of folding in these materials and the feasibility for their modification for electrical conduction.

10:15 AM GG4.5 Hierarchical Self-Assembly Through Electrostatic Interactions, Gerard Kossow, University of Illinois at Urbana Champaign, Urbana, Illinois; Physics, 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. The diversity of interactions is quite general, since all nucleic acids, cell membranes, as well as most proteins and sugars are charged. The interactions which self-assemble are frequently opposite in charge to contrast, 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 length. Fully charged, but oppositely charged complexes can also be formed from 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.

10:45 AM GG4.6 Biomolecular Nanolithography: Scaffold Approaches to Organized Nanoparticle Structures, James. E. Hutchison, Gerard 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, bandgap modulation, capacitance 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 to addressing these challenges 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 mixed-base DNA samples comprised of 250 base pairs (~85 nm) and 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 nanoparticles affects the electronic and optical properties of the nanostructures, and the potential of using specific DNA templates to control the assembly sequence to interface the nanostructures for electrical and optoelectronic applications will also be discussed.

SESSION GG5: Nanowire and Nanotube Assembly
Chairs: Xavier Blase and Mauricio Terrones
TuesdayAfternoon, November 30, 2004
Room 311 (Hynes)

2:00 PM *GG5.2
Monolayers of multwall carbon nanotubes,
Vladimir A. Samulov1, Jean Galibert2, E. Couteau3, M. Seo3, L. Forro2, J. Sokolov2 and M. Rafailovich1, 1Materials Science, SUNY-STM, Stony Brook, New York; 2Laboratoire National des Champs Magnetiques 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 bundles (nanotube mats, networks, etc.) based on highly controlled deposition 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
Atomic Step-Templated Formation of Single-Wall Carbon Nanotube Patterns

Angew. Chem. Int. Ed.

2004, in press.

Spatial Organization of ZnO Nano-Rods on Silver Surfaces.

2:45 PM GG5.5

Electrochemically-addressable biological functionalization of carbon nanotubes and nanofibers. Chang-Soo Lee1, Sarah E. Roush2, Matthew S. Munch3, Mark J. Anderson1, Robert J. Hamers1; 1Chemistry, University of Wisconsin-Madison, Madison, Wisconsin; 2Physics, University of Wisconsin-Madison, Madison, Wisconsin.

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 electrochemical-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.

2:30 PM GG5.5

Spatial Organization of ZnO Nano-Rods on Silver Surfaces.


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. Such an approach is purely additive, i.e. depositing materials only where they are desired, and avoids contaminating the pristine surface elsewhere. 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 step-edges out-of-plane when the crystal morphology and surrounding regions are covered with mercaptoalkanoic acids (HSCnH2nCOOH). 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 patterns over 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 multisite program 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 Effect: The Wetting of Vertically Aligned Si Nanorod Arrays. Yiping Zhao and Jiaguo Fan; Physics and Astronomy, University of Georgia, Athens, Georgia.

The wettable behavior of a solid state surface is affected by both the surface roughness and the type of chemical components. Recent works have shown that nanoscale structures such as polymer fiber arrays and carbon nanotube arrays, which are fabricated by the spreading method, can produce super-hydrophobicity. However, it is a systematic study on the wetting behavior of such nanoscale arrays on the micro scale due to the limitations of the fabrication techniques. Here, we report a systematic investigation on the wettability of vertically aligned Si nanorod arrays with different height (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 de-posited hydrophobic films, there was a contact angle transition from a rough surface to a hemi-wicking porous surface at a certain film thickness which is determined by the nanorod diameter and the surface chemical composition. The observed results can be reasonably interpreted within the framework of the classical Young’s theory. We have also observed that for the hydrophobic nanorod arrays, the spreading of the water droplet deforms the nanorods on the substrate, and generates intriguing percolation patterns that change with the spreading diameter. This so-called nano-carpet effect reflects the dynamic spreading process, and from the deformed nanorods, one can estimate the dynamic capillary interaction between the water and the nanorods. Acknowledgement: Work supported by NSF.

4:15 PM GG5.9
Synthesis and Applications of Hierarchical Nanowire Networks. Donghui Wang, Rong Kou, Maria P. Gil and Yunfeng Lu; Chemical Engineering, Tulane University, New Orleans, Louisiana.

Nanoscale building blocks, such as quantum dots, nanoparticles, nanorods, nanowires, nanobelts, nanotubes, and nanomesh, have attracted tremendous attention due to their peculiar and fascinating properties. It is necessary to assemble low dimensional nanoscale building blocks into a new class of nanostructured systems for the potential applications in energy storage, separation, catalysis, computation, sensing, etc. In this work, we report the synthesis, characterization, and applications of macroscopic hierarchical metal or semiconductor nanowire networks, in which the growth of nanowires is induced by the PbSe nanocrystals in FETs and IR active opto-electronic nanodevices.

4:45 PM GG5.11
Assembly of Silicon Nanoparticles Roll Up Into Flexible Nanotubes. Munir H. Nayfeh1, Sahraou Chiheb2 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 nanoparticles. 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 future enhanced biological recognition and sensing of toxins. Moreover, they are useful as catalysts, and in nano-robotic applications.
developing the outer profile of objects supported on a solid surface. In our initial demonstrations, we formed arrays of silica beads on gold and silver surfaces using means of self-assembled alkanethiols onto these arrays using a planar PDMS stamp. These arrayed beads served as guides to deliver the alkanethiols to the metal surfaces where they reacted to form self-assembled monolayers. These patterned monolayers could serve as ultra-thin resists in a subsequent selective etching process. When silica beads were used as the guides, ring-type structures were formed due to the circular footprints of the beads. Rings with inner diameters from 0.1-0.7 μm and ring widths from less than one μm to greater than one μm have been created by varying parameters such as the diameter of the silica beads, the concentration of thiol, and the contact time of the stamp. This talk will focus on the experimental procedures, capabilities, and limitations associated with this technique. I will also discuss the use of guides other than silica beads, as well as the extension of this technique to smaller scales.

GG6.2

Creating active devices from nanometer sized components requires the precise placement of materials in all three dimensions. Collodially grown quantum dots are typically deposited from solution, using techniques such as spin-casting and drop-casting. These solution-based processes limit the types of substrates on which deposition can be performed, as well as the size of particles made on large-scale substrates. These shortcomings have been addressed by the creation of high performance devices utilizing such nanomaterials. By extending the methods of micro-contact printing and molding to nanocrystal dispersions, we have overcome these obstacles. We demonstrate two dimensional patterned deposition of quantum dots onto diverse substrates, such as silicon, metal, and amorphous organics. This deposition technique has been utilized for the fabrication of bright, uniformly efficient, and color saturated quantum dot light emitting devices.

GG6.3
Novel Technique for Preparation of Dipolar Microparticles by Polymerization of Polarized Emulsions. Vaselin N. Panov1, Olivier J. Cayre1, Hartmut A. Wege1 and Orlin D. Velev2.1Department 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 DC electric field which causes segregation of the positive and the negative surface charges (coming from the cationic and anionic surfactant) on the surface the emulsion droplets. We polymerize the emulsion drops while the surfactants adsorbed on their surfaces are polarized in order to freeze the dipolar surface charge distribution. Thus, we produce a suspension of polymer microparticles of permanent electric dipolar moment. Successful polarization of the surface charges on the particles has been visualized by fluorescence microscopy by using two fluorescent surfactants of opposite charge. Our results show that the produced polymer microparticles retain their polarization when the electric field is switched off for at least several months. Without polymerisation, the emulsion drops quickly relax to uniform surface distribution of the cationic and the anionic surfactant. The use of this method has been extended to core-shell colloids by coating colloidal particles with the polymerisable oil and using the same mixture of surfactants. This has been done with spherical melamine resin particles and polymer microrods. The proposed simple method of dipolar colloid polymerisation allows easy up-scaling to industrial production. Possible applications of these dipolar colloids include photonic crystals with novel symmetries, colloidal substitutes for liquid crystals and water-based electrorheological fluids.

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 (100) 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 nanoinprint lithography. Replicas of the mold in polydimethylsiloxane (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 method could also be used for contact printing of self-assembled monolayers or patterned electrochemical deposition. This bench-top method could be attractive as a highly versatile way of fabricating complex nano-patterns over a large area without the need for an expensive master.

GG6.5
Guided Assembly of Nanoparticles using Nano-templates. Auschwitz Bruno, Xiong Xugang and Jason Small; Nanomanufacturing Research Inst., Northeastern University, Boston, Massachusetts.

Current nanotechnology research focuses on surface modification, matching molecules and "sockets" at the level of manipulating several to several hundred particles or molecules to be assembled into desirable configurations. Commercial scale-up and the promised economic windfall, however, will not be realized unless one can perform high-rate/high-volume assembly of nanoelements economically. Nanotemplates will enable high-rate/high-volume bottom-up, precise, parallel assembly of nanoelements (such as nanoparticles, carbon nanotubes, and polymer nanostructures). The proposed nanotemplates and processes will accelerate the creation of highly anticipated commercial products and will enable the creation of entirely new applications. Although self-assembly of nanoelements may produce uniform patterns or structures, such patterns are difficult to control and manipulate to produce specific design or structures. The proposed nanotemplates, however, will act as platforms or tools to enable the self-assembling of nanoelements into consistent patterns. Some of these nanotemplates can be used as manufactured, but must most be functionalized for ultimate use in nanomanufacturing processes. The nanotemplates used in the templates can be manufactured using e-beam, dip pen, and nanoimprint lithography. The electrostatically addressable nanotemplate offers a simple means for controlling the placement and positioning of nanoelements through conductive nanowires. The nanowires can be manufactured in different patterns and designs using nanolithographic techniques or other self-assembly techniques. Although microchannels and electric fields have been for local assembly of carbon nanotubes for interconnects and electronic devices, these techniques do not provide precise large-scale assembly at high rates and high volumes. The nanoparticles or nanotubes align on the charged wires of the nanotemplate. The nanotemplate and nano-templates can form a device or template function as a template transfer pattern and nanoelements onto another substrate. When the nanotemplates are moved with nano-precision accuracy and alignment, they can be used to deposit a wide variety of nanoelements into very closely packed columns or rows with a very narrow pitch. Preliminary results show the use of nanotemplating nanowires in the guided self assembly of nanoparticles along a 60 nm nanotemplate’s gold nanowires. Using red fluorescent particles show that PSL particles are attracted to positively charged wires only. Techniques have also been developed to prevent or remove any nanoparticles that may deposit anywhere else (other than on the positively charged nanowires).

GG6.6
Nano-patternning of Multiple Self-assembled Monolayers for BioMEMS. Jing 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 numerous 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 EBL-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 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 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 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 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 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 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 composite stamp have been proposed in order to overcome this problem [2, 3].
I'm. However, the of the colloid diameter are required for ICP. Sedimentation on these patterned substrates. This allows local, selective attachment of site-selective deposition of the nanoparticles onto organic monolayer. Simple coating of the solution containing gold nanoparticles and epitaxial assembly of colloidal microspheres during gravity-driven nanoparticles on two-dimensional organic surface templates. Drying followed by solvent-induced lift off. Selective integration of the nanoparticles onto either hydrophobic or hydrophilic region on the substrates. The surface properties of carboxylic acid monolayers attached on gold nanoparticles were used to guide the epitaxial assembly of colloidal microspheres. Circular dichroism (CD) data showed that the crystal structure was defined on the nanoscale by the alpha helical secondary structure of PLL chains. The resultant single crystals exhibited the forms of regular hexagonal lamellae. The phage library with a 12-mer peptide on the surface 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 non-specifically-binding ZnO particles. In comparison to an Au film without the ZnO-recgonizing peptides, the peptide-immobilized Au film showed an intense fluorescence derived from ZnO. It should be noted that the ZnO-recgonizing 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.

**GG6.9**

**Monolayer and Pattern Formation using Colloidal Particles through Self Assembly**

**GG6.10**

**Preferential patterning of metal oxides on metal oxide-recogznizing peptides**

**GG6.11**

**A Mesoscale Template Prepared by the Self Assembly of Synthetic Polypeptide**

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 provides a useful base to template material growth from the nanoscale to macroscopic level. Single crystals of synthetic polypeptide (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 resultants 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 films 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 crystallization 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, Yoshikazu Matsumoto, Futoshi Matsumoto, Kazuyuki Nishio, and Hideo Masuda. Kanagawa 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 various kinds of nanomaterials. Here we report that an ideally ordered single domain hole array structure with uniform straight channels and ideal hexagonal arrangement could be obtained by adding oxidization 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. 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.2 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 200 nm which corresponds to that of the pretexturing master 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 [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 Choj, Jeong-Ho Park, Hye Young Koo, 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. Polymers grown from inside of capsules had an order of magnitude higher molecular weight than 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 Silica or Polymer Microspheres, Si-Ha Kwon, Mal-Hyeok Moon, Yang Dai, David J. Pine and Seung-Kon Lee; Corporate R&D Center, LG Chem Co., Daegu, 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 shrinking technique for producing large quantities of colloidal stable clusters of hard-sphere 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 with the number of monomer clusters (n) less than 1. Despite the differences in particle properties and interactions in the three 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 two-dimensional robust process can be used to prepare clusters with shapes such as doublets, tetrahedra, icosahedra, and others, all of which can be rendered colloidal stable in either oil or water through a simple silica coating technique.

GG6.15
Fabrication of Tailor-made Substrates for Self-assembly of Protein Molecules, Chih-Chen Ahn and Henry W. Zandberg; Kavli Institute of Nanoscience, Delft, Delft University of Technology, Delft, Netherlands.

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 nanotechnologies (“bottom-up” in top-down” processes) to fabricate self-assembly of protein molecules. As top-down 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 a two ligands, in which one is hydrophobic and the other is hydrophilic, ring of alternating composition form and create the nanoparticle core. The sequence of each hydrophobic or hydrophilic region is no more the 6 A wide. Proteins are known to nonspecifically adsorb on surfaces by a mechanism involving conformational changes and maximization of the attractive interaction between the ligand shell nanodomains 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 spectroscopy) between the protein resistance of surfaces coated with these particles and surfaces coated with industrial standards, such as poly-ethylene-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 intramolecular 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. Shyr,,2, Robert A. Barry, Pierre Wiltzius1,1 and Paul V. Braun1,1; 1Materials Science & Engineering, 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 structures 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 DNA. Via hybridization of the matching sequences, we were able to direct the colloid assembly onto the substrate into a variety of patterns, including periodic structures, which were studied through spatial laser diffraction. Fluorescence microscopy confirmed that the nanostructures indeed did occur on the glass surface. These dNA-patterned surfaces were used as a template 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 structures was done using SEM. Finally, in DNA interactions are temperature sensitive, we have investigated the response of the colloidal assembly to thermal annealing.

GG6.18

DNA-derivatized polystyrene nanoparticles were assembled onto DNA-functionalized surfaces in spatially-defined two-dimensional structures 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 DNA. Via hybridization of the matching sequences, we were able to direct the colloid assembly onto the substrate into a variety of patterns, including periodic structures, which were studied through spatial laser diffraction. Fluorescence microscopy confirmed that the nanostructures indeed did occur on the glass surface. These DNA-patterned surfaces were used as a template 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 structures was done using SEM. Finally, in DNA interactions are temperature sensitive, we have investigated the response of the colloidal assembly to thermal annealing.
Physico-chemical effects such as pH, ionic strength, and temperature, on self-assembly and engineered, scaffold-directed 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 approaches 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 generalized 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 standard and non-standard covalent links, type II restriction endonuclease for regeneration of assembled DNA units with non-palindromic cohesive ends. Repetitive coding sequences were successfully constructed in a reproducible and predictable manner without the need for special cloning vectors while suppressing the intramolecular cyclization of multimers that is problematic when longer sequences are constructed. Several amphiphilic repetitive polypeptides were designed, coded, and constructed. Constructed DNAs were expressed in standard and commercially available E.coli expression systems. Results for several key peptides are discussed focusing on those structures with customized length and functionality. The physico-chemical properties of these materials are also discussed within the context of adequate concentration-based method for separation of fibrils and monomers.

**GG6.19 Controllable Growth of Nanowire Arrays in One Dimensional Solid-State Nanoreactors.** Andrei Anatolievich Eliseiev, Kirill Sergeevich Napoliskii, Irina Valerienova Kolesnik, Alexey Viktorovich Lukashin, Yuri Dimitrievich Troyakov and Peter Goerner

1Department of Materials Science, Moscow State University, Moscow, Russian Federation; 2INOVENT e.V., Jena, Germany.

One of the most important challenges in materials science today is the preparation of nanostructures 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 as 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, anodic alumina, etc.). The study represents the formation of magnetic, semiconductor and catalytic nanocomposites based on the metallic (Fe, Ni, Ag, Pt, PtCo, FePt, 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 analysis for direct way to determine using neutron diffraction.** Pedro Armando Ojeda, Dorin Hoffman, Mauricio Terrones, Humberto Terrones, Thomas Proffen

1Department of Chemistry, University at Albany-SUNY, Albany, New York; 2College of Nanoscale Science and Engineering, University at Albany-SUNY, Albany, New York.

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 AI2O3/CuAI2O3 Thin Film Multilayer Structure.** Nitin Chopra and Bruce Jackson Hicks

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 sensors. 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 AI2O3/CuAI2O3 multilayer structure. Such thin film patterning eliminates the necessity for e-beam lithography as the film thickness determines nm-scale line dimensions. 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 88.6 nm were observed for Cu line width of 40, 60, and 100 nm respectively when heated in air at 400°C. Standard deviations are 6.3, 6.3, and 26.3 nm indicating larger line widths allow larger deviation in diameter sizes. The NWs grow with tip diameter smaller than base diameter with an aspect ratio as high as 3, 5, 12 for Cu line width of 40, 60, 100nm respectively. TEM study at 50,000x showed Cu NWs grown at 400°C on SiN4 membrane TEM window as a substrate at 400°C showed presence of defects/dislocations at the base of NWs indicative of role of metal films defects in nanowire growth. The minimal thickness of Cu film for SW 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 Mesoscaled Metal Nanotubes from Lyotropic Liquid Crystal Phases.** Houming Lue, Donghui Wang and Yinfeng 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 metals in the pores of the template membranes either by using pulse voltage electrodeposition for short time periods in nanotube with only 2μm length or by using anodic nanotubes as the mesoscopically nanoporous metal or metal oxide films. In this work, we extend this technique to electrodeposition of metal in nanotubes. We have utilized lyotropic liquid crystalline phases formed on amorphous anodic oxide (AAO) membranes from lamellar lyotropic liquid crystalline phases. The liquid crystalline template 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 mesoscaled template 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 membranes. 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, Deshi Wang, K. Kemna and Z. F. Ren

Physics, Boston College, Chestnut Hill, Massachusetts.

A two-step masking approach has been invented utilizing self-assembly of polystyrene nanospheres to prepare triangular lattice arrays of nanodots of low cost. A multilayer of self-assembled polystyrene 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 technique 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.

Jjakub Rybczynski, Yang Wang, Debasish Banerjee, Dezhi Wang, Krzysztof Kempa and Zhilong Ren; Physics Dept., Boston College, Chestnut Hill, Massachusetts.

Self-assembly process of polymer microcrystals has been proven as a very simple and cost-effective technique for preparation of large-scale pore arrays which can be used for the growth of carbon nanotubes or nanowires with controlled periodicity. The separation of individual nanotubes/nanowires and their arrangement can be modified by the use of different diameter microcrystals, mask heating, a double lithography process or a combination of them. Due to their long-range periodicity these lattices may exhibit interesting optical properties such as photonic bandgap behavior, antenna effect, or lasing action. Recent results of nanotubes and nanowires arrays modifications, and their optical properties investigations will be presented.

GG6.25

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

Pang Qian, Deli Wang, Chen Yang, Zhoshui Zhong and Charles M. Lieber, 1, 2; Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; 2Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Branched 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 nanowires and moreover showed that the density of nano-branched can be controlled in a predictable manner. This technique is also used to grow branched gallium nitride 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. Additional growth of <-111> branched carbon nanotubes and quantum wires with growth axis of <111>. Multiple generations of nanowire branches were grown epitaxially from nanowire backbones with well-controlled composition/doping, and specifically individual silicon-based n-type/p-type nanowires. Branched structures were demonstrated to function as well-defined p-n diodes and junction field-effect transistors. The ability of sequential multi-branched 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.

Travis L. White, 1, 2; Jean-Eric Wogevre, 1, Jean-Francois Doyen, 1, Fahd Huwied, 3, Quang Anh, 2, Cristina Correia, 1, Jean-Marie Padovani 2, Morral Fontcuberta i Anna2, and Didier Pribat 2, 1Laboratoire des Solides Irradies, ECOLE Polytechnique, Palaiseau, France; 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 easily controlled 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 nanostructures have 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 magnetoresistance and thermal effects in nanotransistors. However, one must be careful when applying a third electro. A close enough to the nanowires or carbon nanotubes for an electric field effect. 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 pores parallel to the wire as a template for the synthesis of nanotransistors. The nanostructure 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 nanostructures have 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 magnetoresistance and thermal effects in nanotransistors. However, one must be careful when applying a third electro.
carbon nanotube specimen. Various challenges exist for direct experimental determination of carbon nanotube properties and their interaction with materials and molecules, like integration with high resolution sensors and actuators and firm gripping of the specimen. Additionally, carbon nanotubes embedded in polymer specimen require to perform various kinds of interfacial testing; the information from such arrays is not exploited 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, a large-scale mass production is necessary. One of the key issues impeding the large-scale mass production is the difficulties related to the fabrication techniques for mass-producing devices. A different approach is to go beyond the reliance on conventional fabrication methods now available, such as solution-based approach at low temperature. ZnO nanorod arrays grown vertically from the substrate typically are not compatible with wafer-scale devices. While employing an electric field for selective wire growth directionality, the construction of platelike arrays is achieved by varying the growth conditions. The growth mechanism is analyzed by XRD, transmission electron microscopy, selective area electron diffraction, and X-ray diffraction. A high growth temperature (1000°C), and an appropriate low oxygen to Ar carrier gas ratio, and the ratio of 1:1.63, and a diameter ranging from 50 nm - 300 nm. It was found that the presence of surface oxide powder in the growth experiments was critical. 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 (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. A local catalytic oxidation of CO by Au nanoclusters played a role in accelerating nanowire formation.

GG6.30 Thermally Controlled Growth of Nanowires. Tom Harris1, Debashis Banerjee2, Zhifeng Ren2, and Gang Chen1; 1Mechanical, MIT, Cambridge, Massachusetts; 2Physics, 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 spin-pumping techniques. However, despite the relative simplicity, the 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 nanowires and nanotubes as nanoscale electronic devices is the large-scale controllability of nanowires, as synthesized, which are usually oriented in a random manner. Current methods for producing nanowires are not practical for the mass production of nanowires. A different approach is to exploit the dispersal, separation, and alignment of nanowires by using external electric fields for selective nanowire growth directionality. This method employs a field similar to that used in plasma-enhanced chemical vapor deposition (PECVD) and was the first technique to demonstrate control over the growth of carbon nanotubes and self-assembled nanotubes perpendicular to the substrate.

GG6.31 Carbon-Assisted SiOx Nanowire Growth. Yingping Zhao1, S.-H. Li1, X.-F. Zhu1, Sansuk Pianpanom2, and G.-C. Wang2; 1Physics and Astronomy, University of Georgia, Athens, Georgia; 2Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, New York.

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, Raman spectroscopy, X-ray diffraction, 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 the oxide powder in the growth experiments was critical. 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 (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. 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 Lau1, Yet-Ming Chiang2, and Steve Lustig2; 1Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2DuPont Central Resarch 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 10^7 different 12-amino acid long 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 MWNs (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 nanoscopic 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). Daekyun Jeong, Jaegab Lee, Hyunjung Shin and Jiyoung Kim; 1Advanced 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 it 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 nanostructures. This technique allows to fabricate nanotubes precisely on the control of wall thickness with a few tens nanometers of thickness and a few micrometers of length on soluble nano-templates. We used organic base materials (polycarbonate) nanotemplate supplying uniform nano-scale pores. Then we performed surface treatment using SAM on the nanostructure in order to achieve selective deposition. 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 nanotubes on metal were coated with HDT. We patterned Si/SiO2 substrates using soft contact printing with OTS (Octadecyl-tetrachlorosilane) inks which transfer Si/SiO2 substrate properties from hydrophobic to hydrophilic properties. Hydrophilic SAMs transferred to Si/SiO2 substrate after one step thermal treatment at 1000°C for 10 minutes. We also used nano-templates in direction followed Si wafer line, otherwise there is no nanostructures 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 nanostructures in the direction with FE-SEM and AFM.
GG6.34 Synthesis and Characterization of GaN/InGaN/GaN Radial Core/Shell Nanowire Heterostructures. Silvia Gradecak1, Yat Li2, Fang Qian2 and Charles M. Lieber1,2. 1Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; 2Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Compositional modulation in 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. We report growth and structural investigations of radially-modulated GaN/InGaN/GaN core-shell (CSS) nanowires, whose composition variation can provide bright emission 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 an 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-crystal 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.

GG6.35 Generic Synthesis of Transition Metal Oxide Core-Shell Nanowires. Zirong Han, Chao Li, Zhiqin Liu, Bo Lei, Dahun Zhang and Chongwu Zhou. University of California, California.

A generic non-equilibrium synthesis technique is presented to produce a wide variety of core-shell transition metal oxide nanowires. The key of the technique is the preparation of vertically aligned MgO nanowires to work as the core material. The growth was conducted at 900 degree C on MgO (100) substrates coated with monodispersed gold clusters. Mgo2 powder worked as the feedstock, and SEM images of as grown MgO nanowires revealed that all the nanowires were normal to the substrate. These vertical nanowires were then used as templates for pulsed laser deposition of the desired metal oxides, including YBa2Cu3O6.66 (YBCO), La0.67Ca0.33Mn03 (LCMO), Fe3O4, PbZr0.58Ti0.42O3 (PZT) and Fe3O4. These four material systems represent a broad collection of physical properties, as YBCO is a well-established high Tc superconductor, LCMO exhibits intriguing colossal magnetoresistance, PZT is an important ferroelectric material, and Fe3O4 is a spin half-metal that is under intensive studies. Built upon the knowledge accumulated in the past decades on metal oxide film studies, this technique yielded single crystalline core-shell MgO/transition metal oxide nanowires with precisely controlled layer thickness. Transport studies on a 10 nm thick LCMO nanowire has revealed pronounced magnetoresistance with a transition temperature 170 K and a magnetoresistance ratio approaching 70%. This technique will enable the phase transition studies in nanoscale transition metal oxide nanowires and may pave the way for various novel applications.

GG6.36 Abstract Withdrawn


Abstract: This paper describes a simple and novel procedure for the fabrication of gold nanorods with aspect ratios over 100 under mild conditions. The procedure involves just one-step chemical reduction reaction in which AuCl4- is reduced with sodium citrate in the presence of cetyltrimethylammoniumbromide (CTAB) acting as shape-inducing surfactant. Controlled amount of NaOH must be added into the reaction solution, without which the reduction reaction could not be initiated. After the addition of NaOH, the yellow solution which is characteristic of complex of CTAB and AuCl4- became colorless instantly, indicating the reduction of AuCl4- to Au+. Subsequently, this solution was gradually turned pink, purple and purple-red in a different time period with varying amount of NaOH. At reaction temperature of 80 centigrade, gold nanorods with aspect ratio over 100 could be obtained when the pH value was controlled at about 8.5-10. Lower or Higher than this value could not afford the products of gold nanoparticles with spherical or triangle shapes. We controlled the conditions for the formation of gold nanorods through a process of nucleation and subsequent growth into nanorods with core-shell of CTAB on specific crystalline facets. Key factors, such as temperature, pH value, CTAB concentration and reaction time, are expected to greatly affect the aspect ratio and yield of the gold nanorods. Thus careful control of the reaction condition is important for obtaining target product. The details about the formation mechanism will be presented at the presentation. This process is very simple, without any aid of seeds or additives during the formation process, and expected to be suitable for the large-scale synthesis.


The creation of two-dimensional ordered nanostuctures with precise positional registration on a substrate is important for devices such as patterned magnetic media and plasmonic waveguides. Block copolymers are well-known examples of self-assembling systems, in which chemically distinct phases separate into nanostructured domains. As thin films, these nanostructures can be ideal templates for creating large-area two-dimensional nanostuctures. In this study, we investigate the effectiveness of pattern registration of 2D self-assembled spherical block copolymer polystyrene - b - polyferroencylindimethylsilane (PS) - b - polyferrocenylenylmethylsilane (PFs) arrays formed on substrates with shallow topographical trenches. These shallow trenches act to confine the 29 nm-period polymer spher array within areas with widths from 500 to 5000 nm and lengths of tens of microns. Within each proper trench, well-ordered arrays of spheres form with rows of spheres parallel to the edges of the trenches. (Cheng et al., Advanced Materials 19, 1359 (2007)). In this work we investigate how well the lateral positions of the spheres in the array can be controlled or 'registered' by the introduction of small jams or roughness at the edges of the trenches. The effectiveness of pattern registration was characterized by measuring the translational correlation function of the polymer arrays parallel to the edges of the trenches across large areas. The translational correlation length increases as the trench width decreases from 500 nm to 300 nm, and as the amplitude of the line-edge roughness of the trenches increases. This shows that the stronger confinement of the array that is present in narrower trenches creates better ordering along the unconfined length direction of the groove. In the direction of confinement, the translational correlation length decreases as the direction moves from the edges of the trenches. Models for this behavior will be presented and can be used to design trenches for the registration of nanostructure arrays across large regions of the substrate. A nanostructure array with longer correlation length requires fewer registration marks to sustain global positional registration over a large area. A design window will be given to demonstrate the advantages and the limitations of registering self-assembled nanostuctures using topographical templates.


A novel strategy to synthesize one-dimensional nanoparticles with hierarchical structures is explored. Mesoporous CuFe nanoparticles are used as reaction sources for further self-reorganization processes under judicious control over the experimental conditions, variable advanced shapes of nanoparticles, such as thread, core in shell, wire in tube, particle embedded in wire, have been successfully produced. Possible formation mechanism will be discussed, and unique advantage of nanoparticles as source will be disclosed.
Monodisperse nanoparticles composed of poly(acrylic acid) (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 that interpenetrates the PNIPAM network. The growth kinetics of the IPN particle formation was obtained by measuring the turbidity and particles hydrodynamic radius (R_h) 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 30 OC. 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 very rich phase behavior including a colloidal crystalline phase in which the system displays iridescent colors.


Dispersed in an aqueous solution, gold nanoparticles can self assemble into films at the air interface when another solvent(s) 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 formaing process. 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 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 signals.

SESSION G37: 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 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 important area in materials research will be presented based upon several examples from our work in the Center for Directed Assembly of Nanostructures supported by the Nanoscale Science and Engineering Initiative of the U.S. National Science Foundation. The presentation will include examples of directed assembly of nanoparticles, nanotubes, 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 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 (MPSs) are particularly interesting, by changing the molecules that compose their ligand shell, it is not only possible to change and control the overall material properties, but also to induce given assemblies properties. Here we show how recently discovered mixed monolayer protected nanoparticles, that show ordered domains in the ligand shell,[1] can be chemically modified in specific equatorial spots of their sphere. 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. I A. Jackson, J. Myerson, and F. Stellacci, Nature Materials 2004, 330.


Dielectrophoresis, particle polarization and mobility in alternating electric fields, allows manipulation and control of colloidal particles. We use electric fields to make particle assemblies 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 miniature photonic circuits allowing new approaches for studying the interactions and phase transitions in particle ensembles. Dielectrophoresis can also be used to assemble metallic nanoparticles into electrically conductive microcables. 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 geometry will also demonstrate how by balancing the induced dipole interactions the process can be extended to co-assembly of cells and synthetic particles. The bioconductive arrays obtained by dielectrophoretic assembly techniques can be used as components of sensors and microreactors.

9:45 AM GG7.4 Nanopatterning of Polymer Brushes by Scanning-Probe and Electron-Beam Lithography. Weo Kyung Lee1, Marian Kaholek1, Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, New York.
Sang Jung Ahn1, Kenneth C. Caster1, Bruce LaMattina1 and Stefan Zauchner1; 1Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; 2Biomedical Engineering, University of Michigan, Ann Arbor, Michigan; 3Army Research Office, Research Triangle Park, North Carolina.

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. This approach to patterning gold surfaces in the resulting nanopattern was immediately backfilled with a bromo-thiol initiator and enabled patterned surface-initiated polymerization. In a complementary approach we prepared oxide nanopatterns on resist-coated silicon surfaces by applying a high electric potential between the AFM cantilever tip and the silicon substrate. In this case the nanopatterns were backfilled with a silane initiator SAM. We show that the choice of silane SAM enables both, ring-opening metathesis polymerization (ROMP) and surface-initiated polymerization (ATRP). We also used lift-off (dissolution) e-beam lithography (EBL) to generate gold nanopatterns that could again be used to immobilize a thiol initiator. The resulting patterns are then amplified by surface-initiated polymerization (bottom-up) from immobilized thiol initiator. We demonstrate that by choosing an appropriate nano-lithography 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 interfacing 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 nanoparticulate macromolecules on hydrophobically modified surfaces in the nanometer scale enables fabrication of smart externally switchable polymer nanoarrays. Such nanostructures can provide sensing functionality within integrated nano-scale bioanalytical devices in which the transport, separation, and detection of biomolecules must be performed in aqueous solutions.

10:00 AM *GG7.5
Surface tension based self-assembly of nano and micro 3D structures. David H. Gracias, Zhuyong Gu, Michael Yang and Yiming Chen; Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

The talk will describe results in the assembly of 3D structures ranging from nanowires to micropolyhedra using surface tension. Nano and micro scale components are fabricated using a combination of conventional and unconventional methods of fabrication. These include photolithography, etch as well as electrodeposition in templates. The components are functionalized using self-assembled monolayers that alter the interfacial characteristics of the components, and they are assembled in a picoliter microfluidic chamber under agitation. Specifically this talk will describe strategies and methods for the assembly of 3D structures with relevance to microelectronics.

10:30 AM *GG7.6

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 concentrated inks that can flow through fine deposition nozzles and yet "set" almost instantaneously to facilitate shape retention as they span gaps in underlying layers. Complex 3-D structures with feature sizes ranging from 6.5 to 100 microns are produced by direct writing using a 3-axis, motion-controlled robotic stage. These complex 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 Photonicics to Ultrastrong Material and Tissue Engineering. Nichole Alexander Ketov; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan; 2Materials Science, University of Michigan, Ann Arbor, Michigan; 3Biomedical Engineering, University of Michigan, Ann Arbor, Michigan.

Layered nanostructures with high degree of organization can be prepared from polymers and a variety nanocolloids such as nanoparticles, nanowires, nanotubes, clay platelets, and proteins by means of a new thin film deposition technique known as layer-by-layer assembly (LBA). Stacks of layered 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 materials with unique characteristics include optically active 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.
Deviation of less than 10°. The data were therefore consistent with a onedimensional system that is periodic and has a wave vector of 10°.

SESSION GG8: Theoretical Aspects of Structure and Properties of Nanomaterials and Nanoassemblies

Chairs: Arijit Bose and Mauricio Terrones
Wednesday Afternoon, December 1, 2004
Room 311 (Hynes)

1:30 PM GG8.1 Molecular Simulation of Mesoscale Architectures Assembled from Patterned Nano Building Units. Sharon C. Glotzer, University of Minnesota, Minneapolis, Minnesota.

Today, the extent to which one-dimensional building blocks can be engineered has undergone a quantum leap. We are on the verge of a materials revolution in which entirely new classes of fundamental building units will be designed and fabricated with desired features, including programmable interactions for assembly. Already, many proof-of-concept demonstrations exist. For example, synthetic chemistry now provides the possibility of designing molecular and nanocellular 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-organization and 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 mesoscale architectures in model patterned building blocks, and to show how building block shape and topology, pattern anisotropy, and recognition interactions can be exploited to achieve complex mesostructures in two- and three-dimensional structures such as wires, sheets, junctions, and shells. We apply geometric packing rules and discuss their opportunities and limitations for predicting equilibrium structures. We investigate the stability by thermodynamics and kinetics and explore transformations between ordered structures under changes in thermodynamic and external fields. We further investigate via simulation the stability of assembled structures with respect to various fabrication limitations of the building blocks for applications to nanoelectronics, nanocomputation, storage.

1:45 PM GG8.2 Computational Studies of Anatase Nanocrystals. Serban Erdin, Amanda B. Barnes, and J. Woods Halley.

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 10^5 atoms or more. A self-consistent tight-binding (SCTB) method that could be used to treat systems of this size has been characterized 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 for both electronic and nuclear density functional theory using density-functional theory.

2:00 PM GG8.3 Negative and Positive Curvature. Humberto Terrones, Julio A. Rodriguez-Manzo, Florentino Lopez-Urías and Mauricio Terrones.

A one-dimensional tight-binding Hamiltonian in conjunction with the London approximation is used to study uniform external magnetic field effects on different graphitic nanostructures with negative and positive Gaussian curvature. Ring currents and the induced magnetic moment are calculated on coalesced C60 structures (peapods) and coalesced nanotubes (structures containing heptagons, hexagons and pentagons of carbon). It is found that coalesced C60 fullerenes connected along the five-fold symmetry axes and Haeckelites tubes are metallic and exhibit large magnetic moments. These results have important implications in the magnetic properties of corrugated carbon nanotubes (coalesced peapods). The magnetism observed experimentally in rombohedral C60 is also discussed in the context of ring currents generated by the sp2-polymerization of C69. Finally, the possibility of witnessing magnetic interconnection in interlocked graphene layers is also studied.


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 sp^3 hybridization, 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 found in 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 optoelectronic technology, and b) the observed K superconductivity in baryum doped Si-clathrate is found to be an intrinsic properties of the sp3 silicon network. The electron-phonon (e-p) coupling is strong (A > 1) and, in the case of the carbon clathrates, the e-p coupling is shown to be much larger than in the fullerenes. The strength of the e-p 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" (11)2 tensile or shear directions due to the frustration of the diamond-graphite instability by the cage-like structure. This provides a first explanation for the repeated observation that cage-like carbon materials, such as polymerized fullerenes, and "scratch" diamond and provides new criteria for realizing ultra-hard materials.

3:00 PM GG8.5 Negative and Positive Curvature. Humberto Terrones, Julio A. Rodriguez-Manzo, Florentino Lopez-Urías and Mauricio Terrones.

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This talk focuses on characterization of the thermodynamics properties of three thin film systems including metals nanostructures, ultra-thin polymer layers, and self-assembled monolayers (SAMs) by measuring $C_p$ via nanocalorimetry MEMS devices [1, 2]. We first discuss the measurement of glass transition temperatures ($T_g$), which consist of self-assembled indium clusters whose melting temperatures $T_m$ are strongly influenced by size. $T_m$ decreases linearly with curvature $(1/r)$ as does the value for the heat of fusion. We also found multiple peaks in $C_p(T)$ at regular temperature intervals, which can be related to quantized increments of size - one monolayer of atoms[3], a phenomenon analogous to the "magic numbers" distributions observed in cluster beams studies. The second material system is the size-dependence of glass transition in thin spin-cast polymer films on a platinum substrate[5]. We observe (unexpectedly) pronounced glass transition at thickness as small as 1.3 nm. The glass transition is assigned via the limiting fictive temperature $T_f$ and is found to be almost size-independent ranging from 1000 nm to 3 nm. The evolution of transition is discussed in terms of broadening of transition dynamics. The strength/contrast parameter of the transition remains strong throughout the thickness range and decreases with a characteristic length-scale value of about 1 nm. The third material system discussed is SAMs[6]. We observe the melting/order-disorder transitions of 2D and 3D C10 SAMs grown on polycrystalline Au surfaces via $C_p$ measurement. The amount of SAMs is typically in the 10 picomole range. The transition for the 2D SAMs occurs over a broad temperature range ($100^\circ$C) with a transition temperature $T_m$ of about $70^\circ$C. 2D SAMs, in their as-deposited state before desorption, have an even larger $T_m$ of approximately $200^\circ$C. The heat of melting is about $20 \text{kJ/mol}$, even larger than $T_m$ of $125^\circ$C. The heat of $T_m$ of SAMs grown on Au nanoparticles are comparable to earlier studies using conventional calorimetry.[1] M. Y. Efremov et al., "Ultra-Sensitive Thin-Film Differential Scanning Calorimeter", Rev. Sci. Inst., 73, 179 (2002).[2] A. A. A. Alivie, G. A. Bialek, "The Deposition and Operation of a MEMS Differential Scanning Nanocalorimeter for High-Speed $C_p$ Measurements of Ultra-thin Films", IEEE J. Microelectromech. Sys. 13, 355 (2003). [3] M. Y. Efremov, et al., "Discrete Periodic Melting Points in Nanocrystals", Phys. Rev. Lett., 87, 2560 (2001). [4] M. Zhang, et al., "Melting Point Depression of Nanostructures using Nanocalorimetry", Phys. Rev. B, 62, 10548 (2000). [5] M. Y. Efremov et al., "$T_m$ of ultra-thin polymer films", Phys. Rev. Lett., 91, 85703 (2003).[6] Z. S. Zhang et al., "C$_2$ Measurements of Cu SAMs on Polycrystalline Gold", Appl. Phys. Lett., 84, 5198 (2004)

4:00 PM *GG9.2 Microstructure Evolution and Materials Synthesis in a Self-Assembled Mixed-surfactant Mesophase, Arijit Bose, 1Chemical Engineering, University of Rhode Island, Kingston, Rhode Island; 2Chemical Engineering, Tulane University, New Orleans, Soniana; 3Chemistry, Tulane University, New Orleans, Louisiana. Soft nanoscale materials, such as micelles, vesicles, micromulsions, liquid crystals and other complex fluids are becoming increasingly important from both a scientific as well as an applications perspective. Visualization of these materials is a challenge because of their size, (2 to 100 nm), their low density and their aggregation and morphology is critically dependent on solvent concentration. Soft materials are of particular interest for 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 micromulsion to a gel phase has been observed by increasing the water content of a system consisting of AOT and lecithin 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 contents and temperatures. 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 several opportunities for template-directed materials synthesis, and several examples will be shown.

4:30 PM GG9.3 Formation of Ceramic Nanosheet Using Water Layers in Lamellar Phase As A Reactive Confined Field In Situ Measurement of SAXS by Synchrotron Radiation, Motomu Adachi, Institute of Advanced Energy, Kyoto University, Uji, Japan. Mixed solution of surfactant (Alkylammonium (AA)) and metal-alcoholate (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 TiO$_2$, SiO$_2$, and GeO$_2$ were 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 GeO$_2$ nanosheet had tetragonal crystal, which conformed to the square shape of GeO$_2$ 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 mol ratio of Ge/(OEt)$_2$ 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 periods and thickness of the lamellar phases were almost constant, being 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% Lorentz distribution after 25 sec to 180 sec from contact. These findings indicate that highly stabilized ceramic nanosheets can be synthesized when the suitable surfactant molecule was chosen.
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 for obtaining ordered mesoporous carbon for hydrogen storage (e.g., 1.2 wt % at ambient pressure and 77 K), catalysts, fuel cells, and other applications.

**GG10.2** Characterization of Polymeric Gratings Formed Under Tensile Stresses. Leonard F. Pease

Recent experiments have shown arrays of polymeric ridges or gratings developed from dispersion of the particulate. These ridges are stable under wafer separation and can be transferred onto a substrate, resulting in fine gratings. We will report on our efforts to characterize this process and the resulting gratings. The ridges only form below the bulk glass transition temperature, brittle polymers including polystyrene and poly(methyl methacrylate) may be used. Electron and atomic force microscopy indicate ridges on one substrate are complementary to and interlocking with those on the opposite substrate. The spacing and interdigitating morphology are independent of the molecular weight. The thickness of the film is the only parameter shown to affect the period; the period scales as four times this thickness. This far periods ranging from 200 nanometers to four millimeters have been achieved. While this is a particularly simple several issues remain. We are currently working to understand what controls the orientation, the fraction of the wafer covered (currently from less than a tenth up to half), and what determines the location of lines that do form. We are also investigating the role of the interface in the development process. Such characterization is necessary before the resulting gratings can find application, which may eventually range from bioscaffolds, to templates for patterning of silicon, and microfluidics.

**GG10.3** Hydrothermal Synthesis of TiO$_2$ Nanosheet by Surfactant-Assisted Hydrolysis of Titanium Alkoxide. Fumin Wang

This paper describes a novel method for preparation of TiO$_2$ nanosheets of quasi-anatase phase. By hydrolysing titanium isopropoxide in a surfactant-containing solution, quasi-anatase-nanosheets have been synthesized by hydrothermal method at low temperature (140 Celsius degree). The structural features of the formed titanium oxide nanosheets were examined by scanning electron microscopy, transmission electron microscopy and electron diffraction analysis. The results are compared with those prepared by existing exfoliation process obtained from layered titane. The prepared nanosheets have a nanosheet gallery of 2 nm and high crystallinity. The electron diffraction pattern corresponds well with the 0.38 nm x 0.30 nm periodicity structure, which reflects the two-dimensional atomic arrangement in the nanosheet. The titanium oxide nanosheets prepared in this process often present as a multilayered structure with TiO$_2$ sheets sandwiched with the surfactant. By removing the surfactant and under the presence of some positive ions, the nanosheets structure can be exfoliated into mono-nanosheets, which resulted in a stable colloidal suspension. The experimental results show that the ratio of surfactant to titanium is an important factor for formation of titanium oxide nanosheet. A threshold of this ratio for making TiO$_2$ nanosheets is determined by an adsorbing amount of surfactant that can cover the nanosheet surface sufficiently. The surfactant plays a role isolating the nanosheets and suppressing the crystallization from quasi-anatase to real anatase phase. After the removal of the surfactant from nanosheet galleries, titanium oxide nanosheets with quasi-anatase phase was promoted and the real anatase nanorods or sheets with nano-scale thickness can be formed as a preferred product in the hydrothermal synthesis. The shape and size of the nanosheets is also determined by the presence and concentration of some positive ions. Furthermore a plausible mechanism was proposed for the formation of quasi-anatase nanosheets in our system.

**GG10.4** Observations of the formation of particulate assemblies from dispersions. Derek Malcolm Holmes

When the liquid is removed from a dispersion of sub-micron particles on a substrate, the in-plane shrinkage that would otherwise occur is constrained. This gives rise to a misfit strain between the particulate layer and the substrate, which can cause cracking of the final body or deformation of the substrate. These effects are commonly interpreted in terms of a stress caused by the misfit pressure that builds up in the liquid leaves. Observations of dispersions cast onto a silicon substrate show that formation of the solid body occurs by the horizontal passage of two fronts from the outside to the centre of the layer. To investigate the processes that occur on each side of the assembly, we carried out interferometry method was used to record deformation of the silicon substrates during assembly. These experiments show that the build up of deformation across the plane of the substrate is not uniform, and that the deformation is related to the localised misfit strain associated with the passage of the two fronts. The magnitude and distribution of the misfit strains and hence the properties of the packed assembly can be influenced by modifying properties of the dispersion, such as the interfacial energies and the particle volume fraction.

**GG10.5** Self-Assembly Approaches to Organogel Construction. David W. Brit, Harshil Dhruv and Matt Draper

The ability of fatty amines and fatty acids to spontaneously self-assemble to form gels in water/alcohol co-solvents was investigated as a means to construct highly networked mesoscale architectures having high surface areas for potential use in protein and whole cell sensing and separation processes. Gel architecture and mechanical properties could be dramatically varied through selection of alcohol (methanol, ethanol, or propanol). The ratio of water/alcohol was also systematically varied to optimize gel formation, which only occurred for mixed aqueous/organic solvents. Gel formation could be further enhanced by introducing lactose as a gelling agent to improve miscibility of the system, presumably through formation of hydrogen bond network bridging the surfactant head-groups. Interestingly, lactose lowered the gelling temperature of the fatty acid system, while raising the gelling temperature of the fatty amine system.

**GG10.6** Microspheres Prepared by Sonication-Induced Assembly of Mesoporous Silica Nanoparticles. Philippa Jill Meadows

The ability to control the arrangement of nanoparticle building blocks to higher-order three-dimensional structures is desired to fabricate new synthetic materials with advanced structures and functions. In this work we have explored the sonication-induced assembly of mesoporous MCM-41 silica nanoparticles to produce microspheres with different morphologies, functionalities and porosities. Initially, cationic CTAB and anionic SDS micelle-soluble mesoporous-silica-microspheres were employed and the resulting microstructures were investigated by scanning electron microscopy. SEM images showed the formation of solid spheres, 1-2 mm in diameter, composed of closely packed MCM nanoparticles. Furthermore, microsphere preparation was extended to include amino and thiol functionalised silica nanoparticles with similar results. Microspheres were formed when microsphere volumes of a concentrated suspension of nanoparticles were sonicated in a large volume of toluene at low temperature. The plausible mechanism involves the dispersion of water droplets in the oil phase, which then act as emulsion templates. The hydrophilic silica nanoparticles self-assemble in the aqueous phase and form solid spheres as a result of the dissolution of the water in toluene. In other parallel experiments, it was found that the introduction of cationic and anionic surfactants greatly influenced the structure of the resulting aggregates, in some cases creating perforations in microspheres. These appearances as circular apertures on the surface and spherical cavities throughout the structure and were attributed to the presence of sub-micron sized oil droplets within the dispersed water drops, which are stabilised by the surfactant. Building blocks with a negatively charged surface such as thiol functionalised and calcined particles interacted with anionic SDS to yield microspheres with multiple perforations. However, using cationic CTAB led to raisin-like structures due to the charge mismatching, causing particles to remain at the water/oil interface forming a skin, which crumpled on dissolution of the water. Conversely, with amino functionalised particles, introduction of cationic CTAB gave solid microspheres with perforations since the positive amine takes place and the fronts grow through the dispersion, the through-thickness shrinkage was measured by laser extensometry. The results show that assembly of initially dispersed particles into a packed layer occurs at the first front, and the second front is associated with further liquid held up in the packed body. This is consistent with previous results. An optical interferometry method was used to record deformation of the silicon substrates during assembly. These experiments show that the build up of deformation across the plane of the substrate is not uniform, and that the deformation is related to the localised misfit strain associated with the passage of the two fronts. The magnitude and distribution of the misfit strains and hence the properties of the packed assembly can be influenced by modifying properties of the dispersion, such as the interfacial energies and the particle volume fraction.
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.

Matthew M. Yuen1, Stephanie Loo1, Chun-Xiong Lim1, Jin Luo1, Zia Rab1, Navaid Khan1, Daniel Rabinoivich2, Tanbo Liu3 and Chuan-Jian Zhong1.


The ultimate exploration of nanoparticles in nanoelectronics, information storage, quantum computing, and chemical/biological sensors will depend on the ability to precisely assemble nanoparticles in controllable shapes 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 tetraalkylammonium bromide templating 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 microscope. Potential applications of the nanoparticle assemblies in sensors, catalysis, and nanoelectronics will also be discussed.

**GG10.8**

Periodic Array Nanostructures Using Colloidal Particle Lithography. Hyunjung Shin1, Changdeuck Bae1, Jinho Moon3 and Myung M. Sung2.

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

In this work, we demonstrated a new preparation method of nanoscale periodic colloidal structures with hexagonal 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 followed by hydrofluoric acid etching of SiO2 formed Si substrate. Atomic force microscopy (AFM) allows to fabricate the periodic array of isolated nanostuctures 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 Supriya1 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 amineterminated 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-hexanediol and colloidal gold solution. The resistance of the films after the deposition of 10 bilayers was ca. 1 MΩ. The films were heated at 9 different heating temperatures, 120°C, 160°C, and 180°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 took longer times at lower temperatures. X-ray photoelectron 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 microscope 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 thiol 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 devices 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.

**GG10.10**


Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

In recent years, there has been a great interest in the synthesis of mesoporous carbons because of their unique structures and properties. Various types of mesoporous carbon materials have been fabricated using a complicated templating synthesis method. This method allows precise pore-structure control through replicating the mesostructure of the silica templates. However, the complicated multi-step 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 nanotube 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, 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, phosphorus-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**


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 energies. Calculation of the 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.

**GG10.12**


Chemical 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 oxide, combination of transition metals (TMs) sol-gel chemistry with templating approach is more difficult to master due to the poor sol-gel reactions of transition metal alkoxides. 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...
homogenous TiO2 precursor and colloidal silica template. During the aerosol process, solvent evaporating from the droplets enriched the nonvolatile components and resulted in co-assembly of TiO2 and colloidal silica into spherical particles. Subsequent crystallization of TiO2 and removal of colloidal silica resulted in mesoporous anatase TiO2 particles. The second route to the synthesis of mesoporous TiO2 was using one-step hydrothermal treatment (TiCl4) hydrolyzed in the presence of surfactant (e.g., F127) under hydrothermal condition in absolute ethanol, resulting in mesoscopic crystalline structure. Mesoporous anatase TiO2 particles were obtained after one-step hydrothermal treatment and removal of surfactant by extraction. Particles obtained from both approaches exhibited high surface areas and crystalline (anatase) structures based on nitrogen sorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction measurements. These mesoporous anatase particles are of great significance for photocatalysis and other applications.

GG10.13  
Surface Sol-Gel Modification of Mesoporous Silica Materials with TiO2 for Assembly of Ultra-Small Gold Nanoparticles.  
Nenfo Yang, Bei Chen, Shannon Mark Moharram, Edward W. Hagaman, Sheng Dai and Steven H. Overbury; Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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 inorganic silica surface through the reaction of a high density of silanol groups with functional organic or inorganic species. The fabrication of mesostructured non-siliceous solids has extensively exploited. Herein, we applied a hydrolytic surface sol-gel process, a technique developed by Usui to fabricate metal-oxide thin films with thickness control to nanometer precision on a flat substrate, on the modification of the surface properties of mesoporous silica materials. This technique generally consists of two half reactions: (i) non-aqueous condensation of metal-alkoxide precursor molecules with surface hydroxyl groups and (ii) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxyl groups. The one-layer film growth is achieved by repetition of saturated adsorption of alkoxides and subsequent regeneration of a uniform hydroxyl surface. By using this layer-by-layer approach, one layer of a high-isoelectric point oxide component titanin (86.0) was introduced on the mesoporous silica (SBA-15) surfaces under an atomic-level thickness control and excellent uniformity to decrease the negative charges of silica surfaces. BET analysis indicates that the pore size distribution is decreased from 7.4 to 6.0 nm for the first cycle and 6.0 to 4.7 nm for the second cycle. The reduction of the mesopore size for each cycle should be about twice the single layer thickness. Accordingly, the effective single layer thickness is about 6-7A. The gold precursors were readily introduced via the deposition-precipitation method on the surfaces of the modified mesoporous materials. The subsequent reduction of the surface immobilized gold precursors with Au commercial nanocrystalline titanium support (a) in 7.4-1.0 M H2O2, (b) in 10 K used the mesoporous silica template, was used to gold nanoparticles assembled inside ordered mesopores. Z-contrast transmission electron microscopy (TEM) image of the resulting materials shows the tiny uniformly bright spots (5-10 nm) along the mesopores. The activity of the gold catalysts for CO oxidation was characterized. Comparisons were made between the Au/monolayer TiO2-SBA-15 with Au/commercial nanocrystalline titanium support (using the PtO2/SiO2 as a control) with similar high surface area (i.e., achieving 500% CO conversion above 40°C) were found for Au catalysts on an untreated support. High temperature (390°C, 30 min) 85% He treatment dramatically decreased the activity of nanocrystalline TiO2 supported catalysts, as the light-off curve shifted to high temperature. By contrast, the activity of the monolayer catalyst did not change significantly, achieving >50% CO conversion at 25°C.

GG10.14  
Control of Molecular Orientation of Phthalocyanine Films by using Ultrathin 3,4,9,10-Perylene Tetracarboxylic Dianhydride Template Layers. Takeaki Taboaka, Shunsuke Kawai, Jo Shull, Pan Ho, and Takeaki Taboaka; Institute of Applied Physics, University of Tsukuba, Ibaraki, Japan.

The molecular orientation in thin films of organic semiconductors dominates optical and electrical properties, and the performance of organic semiconductor devices would greatly depend on the molecular orientation and regularity. Most of the organic semiconductor molecules, especially those of high molecular weight, tend to incline their molecular plane away from the several kinds of substrates surfaces such as glass and conductive oxides. It is important to develop a control technique of molecular orientation. In this work, we studied the effects of surface modification of glass substrate on the molecular orientation of phthalocyanine (H2Pc) films. It is well established that the molecular orientation of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) is parallel to the surface of glass substrates, therefore, the surface modification of the glass substrate was carried out by depositing ultra-thin H2Pc and PTCDA layers on glass substrates. H2Pc and PTCDA were deposited on glass in the presence of surfactant (e.g., F127) under X-Ray Diffraction (XRD) which provide the lattice periodicity parallel to the surface, Grazing Incidence X-ray Diffraction (GIXD) which provide the lattice periodicity perpendicular to the surface, and Reflection Absorption Spectroscopy (IR-RAS) measurements. In case of the deposition of H2Pc films directly on the glass substrate, the diffraction peak appeared at 2θ = 6.8° measured by XRD with 8-26 mode, and by GIXD with d = 2.6 A mode. The 2θ peak represents the stacking direction of molecular plane of H2Pc. Therefore, these results indicate that the molecular plane of H2Pc takes a standing arrangement on glass surfaces consistent with the previous results. Then we tried the deposition of H2Pc on PTCDA template layers. A clear diffraction peak measured by XRD was observed at 2θ, and the peak at 6.8° that was observed in the H2Pc direct deposition disappeared. In the GIXD measurements, the diffraction peak at 27° was not observed. These results indicate the orientation of H2Pc molecular plane turned to the parallel arrangement by the surface modification by PTCDA. In the IR-RAS measurements, moreover, the peak of C-H bending vibration at 740 cm^-1, which is allowed at parallel arrangement by IR-RAS selection rule, was enhanced remarkably in the H2Pc on PTCDA structure. These results also indicate the orientation of H2Pc molecular plane turned to the parallel arrangement. In conclusion, it is suggested that the molecular orientation of H2Pc could be controlled by the fabrication of the substrate surfaces and can be controlled by a modification of the substrate surface.

GG10.15  
Multilayer construction of mixed ligand-protected CdS nanoparticles through covalent bond-forming reaction.  
Takahiro Tanaka, Kenzuke Akamatsu and Hidemi Nawate; Konan University, Kobe, Japan.

Ligand-protected nanoparticles consisting of semiconductor cores surrounded by organic monolayers have attracted considerable interest for applications in materials 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 composite 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-mercaptol-1-undecanol was partially incorporated by a place-exchange reaction, thereby providing stable, mixed monolayer-protected CdS nanoparticles. The reactivity of surface hydroxyl groups was verified by a reaction with isocyanate-bearing molecules that provide high carbamate bonds in high yields at ambient temperature. The obtained mixed monolayer-protected nanoparticles were successfully immobilized on a glass substrate through a carbamate bond-forming reaction that could be further utilized for multilayer construction in a layer-by-layer fashion.

GG10.16  
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, nanorreactors, electronic and photonic function devices, low-dielectric constant films, and hosts for high density storage of information. Mesoporous silica films with different pore sizes and structures were prepared by using cationic surfactants (DTACl and CTACl) or PEG-POPC-trilob copolymers (Pluronic F68, Pluronic F127) as surfactant structure directing agents with tetramethyl orthosilicate (TMOS) as silica source. The mesoporous structures of thin films were controlled with the ratio of amphilic halide surfactant and tetraalkoxysilane. They were synthesized by an evaporation-induced self-assembly process and spin-coated on Si wafer. A cumulative heating procedure that controlling agents with tetramethyl orthosilicate as silica source. The mesoporous structures of thin films were controlled with the ratio of amphilic halide surfactant and tetraalkoxysilane. They were synthesized by an evaporation-induced self-assembly process and spin-coated on Si wafer. A cumulative heating procedure that
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 deposited 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 such as pore size, pore structure, and hydrophobicity 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 materials. The surface layers of nanoparticle 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 multilayer mesoporous silica films are made of well-controlled and ordered porous 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 X-ray diffractometry, 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 10 nm were confirmed by TEM. Gg10.17
Bi metallic Nanoparticles: Preparation using Phase Transfer Method and the Study of their Properties. Shweeta A. Shetty1, Sampath S.2, Kamanio Chittappadhyay1 and Rechnam1. 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 alkanethiols as capping agents. The evolution of alloy particles during synthesis is studied using transmission electron microscopy (TEM) to see whether the form core/shell metallic 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 nanoform 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 nanoscale fiber templates. 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 surface properties of the fibers 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 Generate Field Effect Transistors. Liang-Yi Chen, Hsiao-Chiu Hsu and Chau-Nan Hong; Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan.
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 105 and 106 V/m. SEM analysis reveals 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 assemble 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 nanoscale building blocks and manipulation of individual components. Here we report a simple approach to actively control the formation of the self-assembled colloidal crystals in the microfluidic networks. Utilizing a combination of electrophoretic forces and evaporation induced self-assembly, it is possible to actively control the self-assembly process of the colloidal nanoparticles to form colloidal crystals inside the microchannel network. Using this approach, we can not only selectively fabricate the colloidal crystals in the desired channels, but we can also build colloidal crystals with different optical properties in different channels or in the same channel. This method is not limited to the fabrication of 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, Guangyi Han and Liangzhi 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 tartaric 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 nanoparticles form colloidal crystals inside the parallel lines, and the distance between the neighbor lines is around 35nm. On the polished Si surface the nanoparticles formed compact domains. In each domain the particles are close-packed in a two-dimensional hexagonal superlattice and are separated by uniform distances. The pattern variation of the gold arrays is due to different surface characteristics 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. Jingjiao Dai1, Shuangang Huang2 and Mark Rice1,2; 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 energetics 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 force within the meniscus region at the solid-liquid-air interface determines the deposition of the suspended nanoparticles to the substrate. In this geometry, the horizontal orientation of the meniscus results in the formation of a nanoparticle wire. Removing a small amount of 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, electrode writing, a sharpened wire is pressed against the backside of a substrate floating on a...
nanoparticle suspension, thereby imposing an localize 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 metal films. The metal was formed by electrodeposition. We anticipate that electrical interconnects can be formed between planar circuit elements using these deposition approaches.

GG10.23

Oriented Attachment Growth of BaTiO3 Nanoparticles. Songhak Yoon1, Namsoo Shin2 and Sunggi Baik1; 1Materials Science and Engineering, POSTECH, Pohang, South Korea; 2Pohang Accelerator Laboratory, POSTECH, Pohang, South Korea.

BaTiO3 nanoparticles are synthesized under N2 atmosphere at low temperature (<80°C) by the hydrolysis and condensation of barium hydroxide hydrate and titanium (IV) isopropoxide. It was found that synthesized primary particles were aggregates of nanosize nuclei. The binding of hydroxyl ion or water in nuclei leads to the oriented aggregating attachment resulting in primary nanoparticles of a few tens to hundred nanometers. Adjacent BaTiO3 nuclei aggregate to a common micelle only to eliminate high energy surfaces. The size and shape of the aggregates varied depending on the reaction temperature, molar concentrations of precursors, and amounts of water added in the solution. Electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) were used for composition analysis and X-ray diffraction (XRD) for structural analysis of nanoparticles. Morphology development and growth processes were characterized by means of high resolution transmission electron microscopy (HRTEM). Oriented Attachment is a dominant mechanism in early stage of crystal growth and subsequent microstructural development of BaTiO3 nanoparticles.

GG10.24

Thermal and Mechanical Properties of PMMA/Silica Nanocomposites with Controlled Nanoparticle/Polymer Interface. Junghoon Lee1, Robert C. Haddon2, Paul V. Braun3, Brian C. Benicewicz2 and Linda S. Schadler3; 1Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; 2Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 3Chemistry, Rensselaer Polytechnic Institute, Troy, New York.

Previous work with PMMA/alumina nanocomposites has indicated that both the filler size and the nature of the nanoparticle/polymer interface are important in determining the thermal and mechanical properties of the composite. A poor interface between the filler and matrix resulted in an order of magnitude improvement in ductility and a 20 degree decrease in glass transition temperature. The nanoparticles used in this study showed a broad size distribution and it was hypothesized that the large interfacial area provided by the smaller particles caused the decrease in glass transition temperature whilst void generation at the larger particles resulted in a failure in the stacking mechanism from crazing to shear yielding. To test this hypothesis PMMA/silica nanocomposites were made by an in-situ polymerization method using monodisperse nanoparticles whose surfaces had been treated such that control over the polymer/nanoparticle interface was obtained. Composites were made using 15 and 150 nm monodisperse nanoparticles with fluorinated or methylated surfaces. This paper will report on changes in ductility and glass transition temperature in these well-controlled samples. Initial results confirm the decrease in glass transition temperature in the composites with small particles, but not in those with large nanoparticles.

GG10.25


A means will be presented to produce nanoporous hydrogels through block copolymer templating. Micellar solutions of block copolymers of poly(ethylene oxide) (PEO) and a degradable component are cross-linked in a vacuum 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 these materials before and after degradation show order on the scale of 1-100 nm. This method 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 hydrogel 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 nanoporous PEO hydrogels should have chemical functionality in the pore-bound 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 Polyppyrole and Poly(3,4-ethylenedioxythiophene) Nanotubes and Nanowires. Byoung K. Kim1, 2, D. S. Han1, D. S. Suh1, S. J. Lee1, H. M. Kim1, Jinsoo Joo1, Haeyong Kang2 and Won Kang2; 1Physics, Korea University, Seoul, South Korea; 2Physics, EwhaWomans University, Seoul, South Korea.

Nanotubes and nanowires of poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized by using nanoscopic template through electrochemical polymerization method. Dodecylenesulfonic acid (DDSA) acid or tetraethylammonium hexafluorophosphate (TBAF6) 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. Tube of tube or wire and the length including diameter of the system were determined by the synthetic conditions, such as applied current, doping level, and polymerization time. The dc conductivity (σdc) of one strand of PPy-TBAF6 nanotubes treated with HF dissolution was measured to be 2x10^-1 S/cm by using four-probe method, while that treated with NaOH dissolving solvent was 4x10^-2 S/cm. The σdc of PEDOT-DDSA nanotubes treated with HF solvent was 10 S/cm, while that treated with NaOH solvent was 2x10^-2 S/cm. The electrical properties varied with the use of different dissolving solvents to remove the template. The sdc and I-V characteristics as a function of temperature were measured on photolithography pattern from 300 K to 0.3 K. The UV/Vis absorbance and FT-IR spectra of the nanosystems were measured for the optical and structural properties. We observed the dramatic increase of field emission (FE) current by using these nanotubes or nanowires for the nanotip emitters for FE, implying the promising nano materials for FED.

GG10.27

Controlled PMMA Particles Assembly on Substrate by Synchrotron X-ray Using Dispersion Polymerization. Jin Xiao1, Jue-Mok Yi2, Seong Kwon Seol3, Jung Ho Je3, Yung-Chin Yang2 and Yeukuang Hwu2; 1Materials Science and Engineering, Pohang University of Science and Technology, Pohang, South Korea; 3Institute of Physics, Academia Sinica, Taipei, Taiwan.

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 immered in the dispersion media, the size and/or density of the PMMA particles were able to be controlled on selective areas. Interestingly the growth of the particles was occurred 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 designed assembly of PMMA particles in a nano 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. Byoen Moelker1, Nicolas L.Thomass1, Mikhail Artemyev2 and Ulrike K.Wagner2; 1Physics, University Dortmund, Dortmund, Germany; 2Institute for Physico-Chemical Problems, Belozersk, Belarus.

Colloidal CdSe nanorods (NR) and nanodots (QD) are nanomitters 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 CdSe nanorods and nanodots of radii R = 7 and R = 27 nm, respectively, for coupled resonator optical waveguides. Unlike other types of optical waveguides, waveguiding in the coupled-resonator optical waveguide
Shape-controlled synthesis of complex metal oxides nanocrystals as electrosynthetic enhanced assembly to promote the preferential elemental mapping analysis indicates that the negatively charged construction of devices, and the shape of nano-building blocks and correlations between the material properties and its shape. The shape distribution and the dominant polarization type of both the weakly combined with polarization sensitive mode mapping. The spatial coupling with pronounced mode splitting as well as weak coupling coupled microsphere cavities were prepared by impregnating of nanometer unit building blocks is a key process in the design and uniqueness and novelty of material properties. Moreover, the assembly of nanometer unit building blocks is a key process in the design and uniqueness and novelty of material properties. Moreover, the assembly of nanometer unit building blocks is a key process in the design and uniqueness and novelty of material properties. 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Certainly, it is desirable to develop strategies for shape-controlled synthesis of complex metal oxides possessing rich properties, especially the magnetic characteristics. Here we present the combination of monohydrosynthesis 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 coherent phonon sequences of superstructures formed on bi-dimensional shapes of spinel nanocrystals of spinel ferrites. First part is concentrated on the shape-control of monodispersed spinel cobalt ferrite, CoFe204 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 CoFe204 nanocrystals indicate that the blocking temperature, saturation and remnant magnetization of nanocrystals are essentially determined by the volumes (sizes) of nanocrystal shapes. However, the shape of nanocrystals is a dominating factor for the coercivity of nanocrystals. In second part, magnetite, Fe3O4 nanocrystals with truncated tetrahedral platelets (TP), tetrahedral platelets (TP), truncated octahedral (TO) and octahedral (OT) faces were employed 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 superstructures. The formation of the 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-assembled structures of 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/Si(100) with MPTMS [MPTMS: (HS-(CH2)3-Si-(OCH3)3)] and the effect of vacuum annealing on the interfacial adhesion measured by 4-point bend tests. Cu/MPTMS/SiO2 structures annealed to 700 °C show factor-of-9 higher surface energy in comparison to Cu/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 bonding formation between MPTMS/SiO2 interfaces is responsible for improved adhesion enhancements. 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/Ag 3d ratio indicating 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 requirement for integration of thin film devices. References: 1. A. Krishnamoorthy, K. Chanda, S. P. Murarka, and G. Ramanath, J. G. Ryan, Applied Physics Letters, 78, 2467 (2001). 2. P.G. Ganesh, J. Gamboa, A. Ellis, R.S. Kane and G. Ramanath, Applied Physics Letters, 82, 1320 (2003). 3. P.G. Ganesh, A.P. Singh, G. Ramanath, Applied Physics Letters, Article in press.

**GG10.33**

**Engineered Metallodielectric Nanostructures for Novel Sensing Applications**

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The synthesis and characterization of nano- and meso-structured materials capable of detecting changes in their environment with ultra high sensitivities have been receiving much attention over the recent years. There are many challenges for the realization of these systems, such as identifying the underlying physical principles defining the sensitivity limits of given sensor architectures, understanding the operational capabilities of specific materials or structures, and the development and characterization of new materials for integrated nano-sensors. We present here the synthesis and characterization of new metallodielectrics core/shell particles suitable for various sensing applications. Silver nanoshells with controlled grain size and thickness dependently on the surfaces of sub-micron silica spheres via a modified Tollens reaction. The metal-coated spheres are subsequently pressed into pellets, while the electrical resistivity of the composite is monitored. Alternately, ordered opaline structures may be formed via colloidal self-assembly, utilizing the core/shell particles as elemental building blocks. A clear advantage of these metallodielectric structures is that the amount of metal present is determined by the metal shell size and morphology, and not by the complete filling of interiors. The nanoshell structure, which is important for optimizing sensor performance, may in turn be independently engineered through the chemical deposition protocol. Thus we may optimize the nanoshell composition and morphologies for the different sensing applications of interest. These sensing capabilities may be achieved through optical and electrical responses of the assembled materials. We discuss in particular the role of domain walls and reverse-proportionality 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 not penetrated by solvent or binder molecules. Films of 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 = 49%, the lowest reflection ratio = 0.56%).

**GG10.36**

**Sensitivity of Self-Assembled Gold/Alkanedithiol Films to External Hydrostatic Pressure, Keith Higginson, Triton Systems, Inc, Chelmsford, Massachusetts.**

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 inserted deposited on thiolated substrates, and alternate layers of hexanediol or decanediol "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 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, Donggun Jin1, Christos G. Takoudis1, Jie Zhang2, Paul Bruno3 and Dan Gamota3;** 1Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois, 2Motorola Advanced Technology Center, Schaumburg, Illinois.

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. Electrostatically clamped 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++) generated during the electroless plating process appear to act as channels in the effect device towards 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 mm2) between the SAM 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 McGhee, 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 wide film of one semiconductor with 50-500 nm wide films of another semiconductor. We will show that the arrays of pores can be made in thin films of silicon or tin using Nanoporous 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 to the organic-inorganic interface.

GG10.39

Effect of Restructuring, Metal Loading and Catalysis Reaction on Nanoporous Carbon, Ponnniyam Ayappan 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 graphite vaporization. Electron-beam lithography with PMMA and metal lift-off. 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 to the organic-inorganic interface.

GG10.40

Possible Superconductivity in Langmuir-Blodgett Films Based on Diallyldimethylammonium-Au(dmit)<sub>2</sub> salts, Yasuhiro F. Misu<sup>1</sup>, Shin-ichi Morita<sup>1</sup>, Ryo Watanabe<sup>1</sup>, Michio Sugii<sup>1</sup>, Masatao Hedo<sup>2</sup> and Yoshihisa Uwako<sup>1</sup>; Department of Functional Chemistry, Toin University of Yokohama, Yokohama, Kanagawa Prefecture, Japan; <sup>1</sup>Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba Prefecture, Japan; <sup>2</sup>Institute of Materials Program, Arizona State University, Tempe, Arizona.

We have measured the electrical properties of self-assembled epitaxial NiSi2 nanowires (NWs) formed by deposition of monolayer Ni on C(111) in UHV at 500 C. This forms NWs with a 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 phase-breaking and spin-orbit scattering lengths are found to be 45 nm and 3 to 7 nm, at 4.2 K, respectively, similar to values for thin epitaxial NiSi2 films.

GG10.41

Investigation of the Contact Formation Between Macro-Molecular Building Blocks and Mesoscopic Electrode Materials, Neels Dam, Brian Doran, J. Chris Braungard, Martin M. Beerboom and Rudy Schifl; 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 with regard to deoxyribonucleic acid (DNA) on gold substrates, which have been found to be insulating, semiconducting and metallic. It is likely that the various methods and materials used to connect single DNA strands to a macroscopic electrode 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 interfaces, and to determine the charge injection barriers. The technique is based on an established method using photomission spectroscopy and in-vacuum preparation of the to be investigated interface. In-vacuum deposition has been traditionally an issue for large molecules due to the high energies during evaporation from a hot source. We have developed a method based on an established technique using in-vacuum evaporation for effectively preventing in-vacuum evaporation. The technique is based on the experiments is low vacuum (ES vacuum deposition, which allows us to prepare macro-molecular thin films in vacuum without significant contamination. We present first results of this technique being the use of ribonucleic acid (RNA)/metal interfaces, which serve as a model.
formation of 2D compact hexagonal network, 3D supra crystals in...

...superstructures. Systematic investigation was performed to reveal the supercrystalline arrangements of silver nanocrystals. This coherence is system are altered. This anomalous heterocoagulation behavior is of special interest for the formation of ionic colloidal crystals, where a...demonstrate that the nanocrystals are used as mask for lithography...the supracrystallization is manifested by...the shift to low frequency of the Raman peak due to the Lorentz...As example vibrational coherence is discovered in 3D FCC...self-assembled CdSe nanorods and CdSe/CdS nanorod heterostructures were self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanorods 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 GG1: Structure and Intrinsic Properties of Meso Assemblies II
Chairs: Paul Braun and Alexander Wei
Thursday Morning, December 2, 2004 Room 311 (Hynes)

8:30 AM *GG11.1 Intrinsinc Properties of Nanocrystal Self Assembled.
Marie-Paule Platin, 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 supra crystals in...self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanorods 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.

9:00 AM *GG11.2 Ordered and Non-Ordered Heterocoagulation of Ultrathin Particle Systems. Gary R. Maskelyne, W. Craig Carter and Yet-Ming Chiang.
Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2CPCS, Los Alamos National Laboratory, Los Alamos, New Mexico.

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 an increasing heterocoagulate 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 electrostatics 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 Shevchenko and Dmitri V. Talapin.
Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2CPCS, Los Alamos National Laboratory, Los Alamos, New Mexico.

The monodisperse nanocrystals can self-assemble into one-, two- and three-dimensional superstructures. Various magnetic (CoP3, FeP3, Fe203, CoPd2) and semiconductor (CdSe, PbS) 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 Fe203, CoP3, Fe203, PtFe, Fe203, CdSe - Fe203 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 CoP3, PtFe, Fe203 and CdSe nanocrystals have been grown. HRSEM investigation showed the long range ordering of the nanocrystals with the coherence over entire colloidal crystal. Colloidal CdSe nanorods and CdS/CdSe nanocrystal heterostructures were self-assembled into 3D colloidal crystals. Depending on the growth conditions, monodisperse CdSe nanorods 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 of Meso Assemblies I
Chairs: Albert Schenning and Humberto Terrones
Thursday Morning, December 2, 2004 Room 311 (Hynes)

10:30 AM *GG12.1 Self-Assembly and Magnetic Switching of Cobalt Nano-particle Rings. Alexander Wei, Steven L. Trupp and Rafael E. Dunin-Borkowski.
Chemistry, 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 McHugh, Renouf, Maria P. Gil and Xuan Li. Chemical & Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Nanocatalyst materials often show unique and superior physical, chemical, and tribological properties. The promise of nanotechnology is realized 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 nanostructured 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 nanowires 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 use of dynamic polydiacetylene nanocomposites that show reversible dynamic transitions through responsive self-assembly approach.

11:30 AM GG12.3 Surfactant and Polymer Templated Mesoporous Metals in 2 and 3 Dimensions. Martin Gerard Bailey1, Roger Campbell2, Claude Treiner3, Jean Chevallier4 and Francois Dardoz3; 1Center for Materials for Information Technology, The University of Alabama, Tuscaloosa, Alabama; 2Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama; 3Laboratoire Liquides Ioniques et Interfaces Chargees, Universite` Pierre et Marie Curie, Paris, France.

Soft templating using self-assembling surfactants or block copolymer can be used to prepare very high surface area metal surfaces for use as electrocatalysts and as porous electrodes in applications such as 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 typically 2 to 3 times greater than that of the bulk material. 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.


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-oxide (MOM) nanowire. 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. 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-BoTiO3-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
Chairs: Nicholas Kotov and Mauricio Terrones
Thursday Afternoon, December 2, 2004
Room 311 (Hynes)


Supramolecular chemistry, which makes use of self-assembling molecular units, offers an excellent tool to construct cheaply and efficiently electronic components in high functional materials. For example, 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.


The successful application of quantum dots in many device concepts requires the ability to predict 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 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 temperature 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; 121, 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 Franzl, Thomas A. Klar, Stefan Schietinger, Andrey L. Rogach and Joseph Feldman; Physics Department, LMU Muenchen, Photonics and Optoelectronics Group, Munich, Germany.

Motivated by natural antenna complexes and by semiconductor heterostructure lasers, we have introduced the 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-energetic 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 upper-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 be tuned easily by changing 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 across the excitonic 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. Second, there is a clear enhancement of the emission intensity of the largest 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 GC ET 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 microscale. 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 Nanomaterial Properties Switched by Double-Layer Charge Injection and Retained in Vacuum. Dong-Seok Sub1, Alan G. MacDiarmid1, Edgar Munoz2, W. Joshua Kennedy2, Zeev Vardeny3, Anwar A. Zakhidov2, Vladimir Agranovich2, Alan B. Dalton2, Steve Collins2, Mei Zhang2, Von H. Ebron2, John P. Ferrara2, Ali Abe1, S. Lee1 and Ray H. Baughman1; 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 Tang2,2, Guang Yang1, Qi Qin1, Lu-Chang Qin1,2, and Otto Zhou2,4; 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 10° 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 field and mechanical vibration. The CNTs are capable of delivering high and stable electron field emission currents of 3-5 μA (10^4 A/cm^2 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.