SYMPOSIUM C

Anisotropic Nanoparticles—Synthesis, Characterization, and Applications

November 27 – 29, 2000

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*Invited paper
SESSION C1: METALLIC NANOPARTICLES AND CLUSTERS I

Chair: L. Andrew Lyon
Monday, November 27, 2000
10:00 AM *C1.1
ORDERED 3D, 2D, AND 1D ARRANGEMENTS OF Au55 CLUSTERS. Günter Schmid, Monika Blumle, Norbert Beyer Institute for Inorganic Chemistry, University of Essen, GERMANY.

Ligand protected Au55 clusters with a diameter of 1.4 nm have turned out to work as single electron transistors even at room temperature. Consequently these remaining challenges for building blocks in future electronic and optical devices. To reach this goal the clusters have to be organized in well defined structures. 3D cluster assemblies become available in microcrystals with hexagonally packed Au55(PPh3)12Cl6 clusters. 2D Assemblies of naked Au55 clusters are prepared by careful elimination of the ligands of Au55(PPh3)12Cl6 by thiocyanate-functionalized fourth generation dendrimers. Ordered 2D layers of the same clusters can be generated by a self-assembly process at the phase boundary between water and dichloromethane using amphiphilic polymers as structural directors. Hexagonal and square orders are observed. Defect free areas of some nm2 can be generated. The cluster monolayers can be transferred to solid substrates. Among various matrices to generate 1D cluster wires, rigid polymer molecules turned out to work best.

10:30 AM *C1.4
ELECTRONIC AND OPTICAL PROPERTIES OF MOLECUL ARLY-BRIDGED METAL NANO PARTICLE ARRAYS. James P. Novak, Louis J. Broussard, Dan L. Feldheim, North Carolina State University, Department of Chemistry, Raleigh, NC.

Nanometer-sized metal and semiconductor particles (e.g., gold and CdSe) are certain to be important fundamental building blocks of future electronic and optical devices. This presentation will describe both the synthesis of nanocrystals etc., in dilute solution, and how array geometry and interparticle distance is well-defined. Electronic communication between particles in an array is characterized by thin-film nanometre-visible spectroscopy, and hyper-Rayleigh scattering spectroscopy. Prospects for writing single nanoscale metallic/semiconductor junctions will also be discussed.

11:00 AM C1.5

Over the years, much has been learned about the fundamental physics and chemistry of metal nanoparticles embedded in various host materials due to the reduction of their size. Both experimental results and theories have shown qualitative and sometimes semi-quantitative agreements. The challenges remain to precisely control physical parameters such as size, shape (isotropy versus anisotropy), particle number density and composition of the nanoparticles, and to understand the effects from the confining host and structure of the host-guest interface. In this report, we have chosen an intriguing system - gold nanoparticles confined in crystalline MGO to demonstrate how each individual parameter affecting the overall properties of Au nanoparticles by proper simple fabrication, shape and interface tailoring and comprehensive optical and structural characterizations. The techniques include pulsed laser deposition, e-beam evaporation and ion implantation for sample fabrication, thermal and laser treatments for size and shape control, and optical and thermal spectroscopy, TEM and RBS for property analysis.

Depending on the fabrication sample treatment used, a single surface phonon absorption peak of Au in MGO can be tuned from 550 to 600 nm, and/or more than one peaks observed. Thermal and laser treatments can lead to gold nano-cube and nanosphere formation. In addition, it is also shown that the creation of the defects on MGO host matrix can also alter the optical properties of the nanocomposite materials. Theoretical modeling will also be used to evaluate the underlying mechanisms of each individual parameter which is often reported as an ensemble of all the parameters together.

11:15 AM C1.6

State University of New York at Stony Brook, Dept. of Chemistry, Stony Brook, NY, and Brookhaven National Laboratory, Dept. of Applied Sciences, Upton, NY; Louis E. Brus, Columbia Univ., Dept. of Chemistry, New York, NY.

Because of their 5.50 nm size range, nanocrystals are unique in that the number of surface atoms is a large fraction of the total. Hence, their intrinsic properties are transformed by quantum confinement due to the spatial confinement of excitations. Nanomanipulation of nanoparticles (both silver and iron oxide) has been accomplished using the atomic force microscopy (AFM). Using a silicon AFM tip in conjunction with nanolithographic algorithms which are part of the microscope software, we have successfully been able to move and push particles (50-150 nm in size) together in a controllable, reproducible, and nondestructive fashion. The goal initially then has been to obtain Mie scattering on two nanoparticle pairs as a function of their interparticle distance. It is predicted and has been found that the electromagnetic interaction between the irradiated particles strengthens as the particles are brought together from a distance of microns to a point of contact, with noticeable effects on the optical spectra. The second aim of our studies has been to study in great detail the optical spectra of individual iron oxide (hematite) nanocrystals, which are important for understanding the radiative behavior of hematite particles present in atmospheric aerosols as well as phenomena involving the formation of metal oxides such as metal corrosion. Correlations between the peak position and shape of the absorption curves with the nanophotonics of the nanoparticles have been obtained. As expected, the wavelength of the individual Mie resonance shifts red as the particle size increases. The single nanocrystal spectra are far sharper than the extinction spectra of the parent colloid which contains a range of sizes and shapes.
11:30 AM C1.7
ANISOTROPIC Fe/Cr-STRUCTURED FePt NANOPIRATE ASSEMBLY. Shosheng Sun, C.B. Murray, D. Weller, L. Balke, A. Moser.
We present our chemical approaches to anisotropic Fe₃C₆₃₉₃₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈₈¢
SESSION C3. METALLIC NANOWIRES
Chair: Bruce D. Miller, Monday Afternoon, November 27, 2000
Liberty (Sheraton)

3:30 P.M. C3.1
MAGNETOTRANSPORT PROPERTIES OF ELECTRO-CHEMICALLY DEPOSITED METALLIC NANOWIRES
Peter C. Seery, Li Sun, Johns Hopkins University, Department of Materials Science and Engineering, Baltimore, MD; Chih-Lang Chen, Daniel H. Reich, Johns Hopkins University, Department of Physics, Baltimore, MD; G.J. Meyer, Johns Hopkins University, Department of Chemistry, Baltimore, MD.

Long, ultrathin wires may be considered quasi one dimensional and are often referred to as nanowires. Such artificially structured materials may exhibit highly nonintuitive properties in comparison to a bulk film due to the extra degrees of freedom associated with the length scales not present in the film. Further degrees of freedom can be achieved by fabrication of layered nanowires. If the dimensions of the wire diameter or layer thickness become smaller than a characteristic length scale of interest, then significant enhancements in the properties may be observed. The fabrication of nanowire arrays by electrochemical deposition into nanoporous templates formed by nuclear track etching of single crystal mica films will be described. Measurements on single nanowires are carried out using self-assembly techniques from suspensions prepared by stripping the nanowires from the template and dissolving in a suitable solvent. Examples of property enhancements in Ni, Bi, and Cu/Co nanowires will be discussed.

3:45 P.M. C3.2
PREPARATION OF NOBLE METAL NANOWIRES USING HEXAGONAL MESOPOROUS SILICA SBA-15
Yong-Jin Han, Ji Min Kim, Korea Advanced Institute of Science and Technology (KAIST) at Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA.

With increasing miniaturization of electronic and mechanical materials, the field of nanostructured materials has received much attention. Due to their size, nanomaterials exhibit optical, electrical and mechanical properties which differ from the properties of the bulk materials. In general, nanostructured materials have been produced using conductive polymers, metal and semiconductors. Metal nanowires in particular have been the focus of many researchers due to their potential applications in fields such as nanoelectronic circuits and nanochannels. We demonstrate a novel preparation method for the formation of metallic nanowires from gold, platinum and silver using mesoporous silica SBA-15 as a template. SBA-15 controls the size and the growth direction of the nanowires and also prevents bulk aggregation of the metal. Nanowires can be isolated from the silica framework by treatment with HF. Nanowires obtained by this method are homogeneous in diameter and can be synthesized in the ranges of 6 to 30 nm in diameters and have an average length of 0.5 µm.

4:00 P.M. C3.3
MATRIX ASSISTED SYNTHESIS OF PALLADIUM NANOCAVE AND NANOWIRES
J. Kang, H. King, R. Yoon, Department of Chemistry and Biochemistry, Korea Advanced Institute of Science and Technology (KAIST); S.J. Oh, H.-C. Ri, Korea Basic Science Institute, Taejon, KOREA.

Our study describes the synthesis of novel nanoscale Pd cage and wires whose sizes and shapes are templated by mesoporous matrices. The matrices used are cubic phase MCM-48 and hexagonal phase SBA-15, which have pore diameters of 33 nm and 5 nm, respectively. For Pd-MCM-48, the Pd metal forms spherical domains (~3 nm) consisting of three dimensionally interconnected Pd nanowires, while Pd-SBA-15 forms elongated agglomerates (~100 nm) consisting of linear chains of individual Pd nanoparticles. The Pd materials are examined by HRTEM, XRD, BET, EDX analyses. This study elucidates the synthesis of shapes and size-controlled pure-standing Pd nanomaterials and this method can be extended to the synthesis of other kinds of shaped nanomaterials.

4:15 P.M. C3.4
UNIDIRECTIONAL PLASMON PROPAGATION IN METALLIC NANOWIRES
Robert M. Dresner and L. Andrew Lynn, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

We report the observation of unidirectional plasmon propagation in metallic nanowires over distances >10 µm. Through control of the incident excitation wavelength and rod composition, we demonstrate the selective coupling of photons into the plasmon mode of a 20 µm diameter nanowire. This mode then propagates in a nonamissive fashion down the wire length before being emitted as an elastically scattered photon at the distal end. As expected from previous studies of plasmon excitation in nanowires and thin films, we observe strong wavelength and material dependence of this phenomenon. Our self-dependent plasmon propagation exploited to produce a wave through which plasmons propagate unidirectionally. A bismuth telluride wire with a sharp Au/Ag heterojunction is shown to display both wavelength dependence and unidirectionality with respect to plasmon propagation across the heterojunction. It is expected that these results will contribute to the growing interest in optical energy transport in nanoscale and nanoscale devices.

4:30 P.M. C3.5
BAR-CODED METAL NANORODS AS PLATFORMS FOR BIOANALYSIS

A novel bar-coding technology is described that could enormously impact the life sciences or any area in which a large number of samples are to be analyzed. We have adapted technology from the molecular world to the biologically relevant microscopic level. The use of barcodes in bioanalysis has many advantages over current technology: (i) the theoretical number of possible combinations is greater than a million, which stems from the compositions and length of metal segments in the barcode pattern. (ii) Stability for long periods of time has been observed. (iii) "Solution-based" analysis yields increased analyte binding efficiency as compared to planar surfaces. (iv) Different metals can be differentially distributed for multiplexed measurement or for an internal control. (v) Analyte identity can be directly determined by cutting the interogation in real-time. And (vi) quantitation of analyte is possible. This technology exploits the inherent differences in reflectivity of metals, which can be visualized easily using conventional optical microscopy. The composition and sequence of metal stripping pattern can be controlled during synthesis and provides a unique tag for molecule identity (e.g. Au-Pd-Au or Au-Ag-Au-Au). Based on recent chemistry developed through collaborative work, we have shown the ability to produce free-standing nanorods in solution (Martin, B. R. et al. Adv. Mater, 1999, 11, 1021-1025), which renders them useful for bioanalysis. In short, a biopolymer can be performed directly on the rod, with analyte identity provided via the barcode pattern. Barcode rods have been fabricated ranging in sizes from 30 - 200 nm diameters and 0.4 - 8 µm lengths employing various metal compositions, including Au, Ag, Pt, Pd, Ni, Cu, and Co. The data to be presented will focus on concept demonstration employing fluorescent tags for detection of analyte binding to the nanorod, with analytic identity determined via optical readout of the barcode pattern.

4:45 P.M. C3.6
AUTOMATED SYNTHESIS AND APPLICATIONS OF NANO-SCALE BARCODES

Many biomedical applications exist for barcodes that can be utilized as nanoscale barcodes (nanobarcodes). Free-standing, cylindrically-shaped colloidal metal nanoparticles have been previously described, in which metal compositions have been alternated (e.g. Ag-Au-Ag-Au-Ag) along the length, and in which the metal segments can be both lengthened and selectively chemically
functionalyzed with a variety of biomolecules. Differences in metal reflectivity, which can be observed using conventional optical microscopy, can significantly enhance the dynamic range of the microscope. We will describe the development of an automated template-directed synthesis system that has been used to simultaneously synthesize 25 different types of nanorods in 25 different templates. Additionally, image analysis software has been developed to uniquely identify each type of nanorod from microscopic images and to quantitate fluorescence signal from each particle. Data from multiplexed immunoassays will be presented to demonstrate the utility of nanorods in biochemical measurements.

**SESSION C4: POSTER SESSION**

**C4.1 AN INVESTIGATION OF MIXING IN Au/AgX HETERO-JUNCTION NANORODS**

Majda El-Kennedy and Celso A. Reis Jr.
Department of Chemistry, Georgetown University, Washington, DC.

We have electrochemically synthesized nanorods composed of gold and silver halides using a template synthesis technique in a porous alumina membrane. In this set of experiments we have analyzed the optical spectra of composites in which the Au and AgX phases are either in intimate contact or separated. We have been able to separate the Au and AgX nanorods by creating a gap between the two phases that can be varied in size. In addition, a third material (Au2S3) is used to form Au/Au2S3/AuX nanorods. In the case of the Au/Au2S3 rods we observe a broadening of the plasmon resonance and a disappearance of the exciton peak associated with the band edge of the semiconductor. This effect is more pronounced when the two phases are separated. P-polarization tilt studies also indicate that there is some interaction between the metal and semiconductor particles that lead to the observed changes in the optical spectra. Our data suggest that there is possible mixing between the two phases. Computer simulations performed including Maxwell-Garnett and Bruggeman theories suggest that the mixing is on the atomic level and may lower the free lifetime of the metal phase. Mixing does not seem to be a problem with the Au/Ag nanorods since Au2S3 is introduced between the Au and Ag. We attempt to interpret all these results with respect to the intermixing model we have proposed.

**C4.2 SITE-SPECIFIC ATTACHMENT OF GOLD NANOPOLARITIDES TO DNA TEMPLATES**

Karen Stevenson, Govindarajan Muraleedharan, Thomas Thundt, Oak Ridge National Laboratory, Life Sciences Division; Leon Myas, Oak Ridge National Laboratory, Chemical and Analytical Sciences Division; Jacob Burhren, Oak Ridge National Laboratory, Computer Science and Mathematics Division, Oak Ridge, TN.

The need to produce regular arrangements of nanoparticles led to the idea of using DNA as a scaffold or template for assembly of nanoscale arrays. Beginning in the 1980s Seeman et al. experimented with combining DNA segments to produce geometrical shapes, including cubes, triangles, two-dimensional arrays and various forms of DNA knots. Using DNA as a structural molecule has many advantages. It can be easily synthesized in lengths from 5 to over 100 nucleotides. It can be joined end to end to produce longer linear molecules or more complex shapes, and it can be modified at predetermined sites to allow for the attachment of other molecules in a specific manner. We are creating linear arrays of DNA with gold binding sites located at periodic intervals. As a first step, we designed a DNA template with amino modified thymine located every 3.7 nm, which would allow the attachment of carboxylic acid functionalized gold nanoparticles. The gold particles were covalently bound to the amino groups on the DNA using standard EDAC chemistry in the presence of a competitor to block excess gold binding sites. The products were analyzed by gel electrophoresis, transmission electron microscopy and atomic force microscopy. Using this method DNA up to 55 nm long containing about 15 gold particles was produced.

**C4.3 MAGNETIC PROPERTIES AND FREQUENCY BEHAVIOR OF SUPER-FINE Nio.64Co4.36Zn48Fe2O4 FERRITE POWDERS**


Superfine S-type Nio.64Co4.36Zn48Fe2O4 ferrite powders have been synthesized by chemical co-precipitation method. X-ray diffraction and Rietveld fitting were carried out to study the particle structure. The results show that the grain size of the powders can be controlled by different co-precipitation and subsequent sintering conditions. Magnetic properties have been measured using a vibrating sample magnetometer (VSM) with an applied field up to 8 kOe. It was found that the coercivity Hc decreases rapidly with the decrease of Co content and the variation of X did not significantly decrease the saturation magnetization. Magnetic permeability of the powders was investigated by HFS1000B7 analysis in the 9-18 GHz frequency range. The results reveal that the magnetic loss resonance frequency of Nio.64Co4.36Zn48Fe2O4 ferrite powders shifts lower frequency with the decrease of Co content and the increase of powder weight fraction (wt%) in a ferrite powder and proxix wafer matrix.

**C4.4 TETRADECANETHIOL DERIVATISED GOLD NANOPOLARITIDES AT THE AIR/WATER INTERFACE**

H.J. White, K. Shin, M.H. Rassavkhocz, J. Solcova, G. Halada, State University of New York at Stony Brook; R.B. Lenzno, A. Buzin, C.J. Clarke, McGill University, A.J. King, Purdue University, D. Nguyen, B.M. Osco, Brookhaven National Laboratory.

The gold particles (AuCl4) were shown to form a uniform film, with 1.3 micrometer thick when spread at the air/water interface. Grazing incidence diffraction (GID) indicated a mean interparticle spacing of 3.2 nm, which was in good agreement with TEM on LB films. The surface pressure-area isotherms were measured as a function of subphase temperature. Features in these isotherms have been interpreted in terms of structural changes in the film, deduced from the scattering data. Very different behavior of the films was observed above and below the melting temperature of the chains. At room temperature, the films were still becoming very rough compression. Above the melting point one observes a single layer which continuously thickens.

**C4.5 NANOPOLARITIDE-DERIVED ASSEMBLIES: A COMPARATIVE SPM AND SEM CHARACTERIZATION**

Li He, Matthew M. Saye, Chu-Jin Zhong, Department of Chemistry, State University of New York at Binghamton, Binghamton, NY.

The ultimate utilization of nanometer-sized particles in microelectronics, molecular recognition and chemical/biological sensing relies on the preparation of nanoparticle materials with isolated or organized nanoscale structures and properties. This work explores scanning probe microscopy (SPM) and transmission electron microscopy (TEM) to study the formation of nanoparticle assemblies and organizes on different substrates. The basic strategy explores spontaneous core-shell and shell-shell reactivities at thiol-thiol-capped metal nanoparticles. Gold nanoparticles of different sizes and shape properties are used in the nanocryostat cores, and thiols of different functionalities, e.g., thiol, carboxylic acid, and amino acid, are exploited as molecular linkers. The intercore or intershell reactivities involve covalent Au-thiol bonding or non-covalent hydrogen-bonding or electrostatic interactions. While spectrophotometric and漫反射ance measurements provide kinetic estimates of the reactivities, SPM and TEM microscopic imaging measurements of the nanostructures are demonstrated to probe the morphology with different nanoscale capabilities. Investigations of 2D/3D nanostructures are analyzed by a comparative SPM and TEM measurement. The correlation of the nanoscale morphologies of the assemblies with the core size and shape properties will be discussed.

**C4.6 TRANVERSE SUSCEPTIBILITY AND MAGNETIC ANISOTROPY IN NANOPOLARITIDE SYSTEMS**


A radio-frequency (RF) resonant method based on a tuneable diode oscillator (TDO) has been used to investigate the dynamic transverse susceptibility in a number of magnetic nanoparticle systems like γ-Fe2O3, Fe and Ni. The systems range from single spherical particles to nanoparticles with varying degrees of anisotropy having tunneling and cross-shell structures. The nanoparticles were characterized primarily using reverse-micelle techniques while some structures were determined with interferometric lithography. Our unique RF method affords precise tracking of switching and anisotropy fields over a wide range of magnetic fields (0 to 9 Tesla) and temperature (15 to 300K) as the nanoparticle systems evolve from superparamagnetic to blocked regimes. In this systematic study, we present our results and discuss the influence of structural anisotropy on the magnetic switching and switching field distributions. Theoretical models based on Stoner-Wohlfarth coherent rotation mechanism will also be presented. Work at AMH supported by DARPA Grant No. MDA972-95-1-0003.
C4.7 THE MAGNETIC PROPERTIES OF Nd–Fe–Mo–B NANO-
STRUCTURED MAGNETS WITH DIFFERENT α–Fe CONTENT.
H. Z. Cui,1,2,3 X. C. Su,4 X. K. Sun,1,3 L. Y. Xiong,1,3 Z. D. Zheng,1,3 J. Feuchtner1,2,3 J. M. Samwer4.1 Centro de Instrumentos UNAM, Mexico DF, Instituto de Metal Research, Academia Sinica, Shenyang, PR. CHINA.

The magnetic, magnetic properties and coercivity mechanism of (1 - x wt.%) Nd12Fe14B–xMo–B (x = 0 - 50) nanostructured magnets prepared by mechanical milling [MM], have been studied. With increasing α-Fe content, the intrinsic coercivity μr decreases monotonously with the reduced remanence J.r/μr increases, the remanence J.r/μr and maximum magnetic energy product BHmax for the nanocomposite magnets basically increase monotonously due to the exchange coupling between α-Fe nano-grains and their nearest Nd12Fe14B–Mo–B nanograins. On the other hand, with increasing α-Fe content, the crystallization temperature of the amorphous phases prepared by high-energy ball milling and the mean grain sizes of α-Fe increase monotonously, whereas the mean grain sizes of Nd12Fe14B–Mo–B decrease monotonously. The position analysis studies have shown that the position lifetime of τ1 and τ2 of the samples with x = 30 ~ 50 are a little smaller than those of the samples with x = 0 or 17. The value of τ1 increases monotonously with increasing α-Fe content. The smaller values of τ1, τ2 and larger value of τ1/τ2 imply a smaller volume of single vacancy, vacancy-clusters and a more compact structure in Nd12Fe14B–Mo–B type nanocomposite magnets with x = 30 ~ 50 than in the nominal single phase of Nd12Fe14B–Mo–B nanograins with x = 17. The smaller value of τ1 and larger value of τ1/τ2 would be favorable for improving μr of the typical Nd12Fe14B–Mo–B type nanocomposite magnets with x = 40. The reversal magnetization recoil mechanism in the nanocomposite magnets prepared by MM may control the coercivity. The magnetic domain pinning mechanism in the nominal single phase of Nd12Fe14B–Mo–B nano-structured magnets with x = 0 or 17 prepared by MM may control the coercivity.

C4.8 SIZE-CONTROLLED SYNTHESIS OF MAGNETIC NANO-
CRYSTALS AND MULTIDIMENSIONAL ARRAYS. J. Cheon, J. Park, K. H. Lee, Department of Chemistry and Applied Biological Science-BK21, Korea Advanced Institute of Science and Technology (KAIST); S. J. Oh, H.-C. Ri, Korea Basic Science Institute, Taejon, KOREA.

The chemical and physical properties of metals in highly divided forms such as nanoparticles are presently the subject of intensive fundamental research with many potential applications. In particular, these studies concern catalytic, optical, or magnetic properties. Here, we focus on the magnetic properties of Co nanoparticles synthesized by thermal decomposition of organometallic precursors in the presence of surface capping stabilizers. We control the size of Co metal nanoparticles from 2 nm to 8 nm by variation of concentration of stabilizers. Obtained Co nanoparticles are highly monodispersed and have a narrow size distribution. The blocking temperature [T_b] is changed continuously with the addition of stabilizer. Co nanoparticles are ferromagnetic below blocking temperature. The Co particles condense into hexagonal close packed array to form 1, 2D structures. We elucidate the relationship between the size and magnetism in Co nanoparticles in this study.

C4.9 MAGNETIC PROPERTIES OF A THIN LAYER OF ORIENTED

Magnetic ions—Fe, Co, and Ni—have been implanted into the near-surface region of single crystals of Al2O3, and yttrium stabilized zirconia (YSZ). With thermal processing, the implanted species precipitate to form predominantly single-domain, single-crystal ferromagnetic nanoparticles that crystallographically align with the host substrate, thereby forming a magnetically anisotropic nanocrystal composite. In the case of Fe, precipitates were formed in YSZ by implantation of Fe8+ at an energy of 140 keV and a dose of 8x10^{14} ions/cm2, followed by annealing in a reducing atmosphere. Similarly for Co, precipitates were formed in Al2O3 by implantation of Co8+ at an energy of 140 keV and a dose of 8x10^{14} ions/cm2, followed by annealing in an oxidizing atmosphere. For Ni, a dose of 8x10^{14} ions/cm2, followed by annealing in a reducing atmosphere, was implanted in Al2O3 at an energy of 760 keV and doses of 5x10^{10}, 1x10^{11}, and 2x10^{12} ions/cm2, followed by annealing in a reducing atmosphere. Special dimensions for the particle size and layer thicknesses are 10nm and 80nm, respectively, allowing for nearly 100% volume filling in the layer, as measured by RBS/channeling.

C4.10 TRANSMISSION ELECTRON MICROSCOPY AND X-RAY DIFFRACTION. Studies on these ferromagnetic particle layers were conducted in the temperature range of 5 to 300 K and applied fields of 10 kOe using a superconducting quantum interference device (SQUID)-based magnetometer. An analysis of the magnetic properties including coercivity, remanence, and saturation moment will be presented as well as the effects of strain and shape hardening. Additionally, the particle size orientation dependence will be determined by comparisons with Ni precipitates in an amorphous substrate of SiO2.

C4.11 HIGH RESOLUTION TEM STUDIES OF GOLD NANORODS. Miguel José Yucumá, Instituto de Física, UNAM and Instituto Nacional de Investigaciones Nucleares, J.A. Ascencio, P. Santiago and G. Canales, Instituto Nacional de Investigaciones Nucleares, MEXICO.

Gold nanorods were studied high resolution TEM, image simulation and electron diffraction. It is found some FCC nanorods present a complex structure of plasma defect running parallel to the nanorod axis. The detailed atomic structure of defects is discussed. In addition it is found a new kind of nanorod based on a pentagonal multiple twinned structure. It is shown that pentagonal nanorods are the direct result of coalescence of a pentagonal and FCC particle.

C4.12 MAGNETIC PARTICLES AND NANOCOMPONENTS IN RF PLASMAS. Jin Cao, Themis Matsasakis, Penn State Univ, Dept of Chemical Engineering, University Park, PA.

Vic reactions not observed in thermally activated reactors, organic molecules in plasma form solid materials of varying degrees of cross-linking, referred to as “plasma polymers.” They may nucleate to form particles in the low nanometer range, or deposit onto substrates as films. In this work, we report our efforts to study the use of low pressure plasma for particle formation and thin film deposition on suspended particles. Plasma polymer particles are synthesized in a capacitively coupled radio-frequency (RF) Ar/methanol discharge at low system pressure, RF power, and monomer flow rates. A variety of particle structure properties are observed, including monodispersed nanospheres and liquid-like viscous nano-droplets. Styrene in particular is observed to produce hollow nanospheres. By manipulating the process parameters, films of plasma polymers can be deposited onto suspended submicron particles. We take advantage of electrostatic trapping to suspend small particles in plasma for extended periods of time until the desired coating thickness is achieved. Sub-micron silicon particles introduced into a low pressure RF Ar/methane plasma are coated with film whose thickness ranges from 3 to 50 nm. The thickness of the coating is controlled through the reaction time, whereas the properties of the coating are varied by the discharge conditions. We discuss the characteristics of these structures, operating conditions, and proposed formation mechanisms.

C4.13 HIGH SPIN Mn MOLECULAR CLUSTERS: SPIN STATE
EFFECTS ON THE OUTER CORE-LIKE MULTIPLE
STRUCTURES. Arl J. Nelson, J. G. Reynolds, University of California, Lawrence Livermore National Lab, Livermore, CA; George Champley, Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN.

Oxo-bridged manganese polymeric complexes have applications in a variety of technologies, such as molecular-based magnetic materials, nanoscale magnets, catalysis and photosynthetic redox chemistry. The reason that these types of compounds are capable of such important and varied technologies is thought to be because they possess ground states with large spin values. However, the electronic, structural and magnetochemical relationships are not well understood and need to be thoroughly investigated to adequately explain why Mn is such an integral part of so many useful processes. X-ray photoemission spectroscopy was used to study the Mn3+ and 3d and valence band electronic behavior as a function of Mn cluster structural properties, where the cluster size and nuclearity are systematically varied. Results show a chemical shift of the Mn 3p3/2/1/2 spin-orbit pair related to the cluster size and nuclearity. Also, the Mn 3s 7S and 5S final state multiplet components shift considerably since it involves the binding energy of a ligand valence electron. In addition, the branching ratio of the 7S/5S series is related to the 3d-3d electron configuration of Mn. Specifically, these precursors forming Mn3+ were implanted in thin films and the 3d-spin is well correlated with 3d-electrons of parallel spin, while in the 5S state the two spins are antiparallel. Changes in this interelectron coherence are clearly observed in the 7S/5S branching ratio as a function of cluster size.
C4.14 **ANISOTROPY AND NONDIMENSIONALITY IN TIN(II)-STRONTIUM FLUORIDES AND FLUORIDE NITRATES.** Georges Délisle and Alena Piocelets, Concordia University, Dept. of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mass Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

PhSnF$_4$ is the highest performance fluoro-iod conductor and it has found applications in chemical sensors. The highest fluoride ion conductivity is found in tin(II)-metal(II) fluorides, where the metal(II) in a large alkaline earth (Sr, Ba) or lead. In addition, their conductivity is purely ionic, i.e. the transport number for electron is very small ($\tau_e = 0.01$). However, the combination of tin(II) and lead(II) is still too weak in suboxide states, in the same material, results in instability under oxidizing conditions. Tin(II) cannot be eliminated, since we established earlier that it is necessary for enhancing the fluoride ion conduction. It is therefore tempting, in order to maintain the presence of alkali cations, to replace lead(II) by strontium or barium, both of which are very stable in the divalent state, and have no suboxide state. We studied the properties of Sn$_2$F$_6$ in an earlier work. In this work, we have concentrated our effort on the preparation and properties of Sn$_2$F$_6$ and Sn$_2$Sn$_2$NO$_3$F$_2$$_2$H$_2$O, the latter being obtained in some preparations and in some attempts to recrystallize the former. Both materials can be obtained in the form of very highly anisotropic samples. Both give rapidly nanocrystals on ball milling. Their preparation, characterization, and properties will be described, with emphasis on the anisotropy and the formation of nanoparticles.

C4.15 **MOLECULAR MORPHOLOGIES IN NANO-FILLED POLYMER FILMS.** Vincent Perreiro, Jack F. Douglass, Archie P. Smith, Alangir Karim, Polymers Division, NIST, Gaithersburg, MD.

We investigate the influence of montmorillonite-chy filler on the morphology of polyethylene oxide, PEO / poly(methyl methacrylate), PMMA blends films formed by spin casting from chloroform solution. After all substrates, the absence of any clay filler, we observe a paper-like morphology when the composition is relatively richer in PEO, relative to the critical composition phase separated morphology observed for PMMA-rich films. Addition of the clay filler has a dramatic effect on the blend film morphology. A transition from paper-like to a "denser" structure similar to "cross" like to an axially symmetric dendritic structure is observed with increasing PMMA concentration of the blend. We are investigating the effect of other fillers (nanotube, dendrimer) on the morphology and the properties of the films. The nanomechanical properties of coated films have been obtained using atomic force microscopy by analyzing force curves.

C4.16 **STABILIZATION AND SEGREGATION OF GOLD NANO- PARTICLES USING POLY [METHYL-PHENYL-PHOSPHAZENE] DERIVATIVES AND GRAFTS.** John V. St. John, Patty Wisn-Nelson, Caroline Walker, Southern Methodist University, Dallas, TX.

Poly(methylphenylphosphazene), PMPP, is one of a unique class of inorganic polymers with alternating (P-N=P) backbones. The reduction of gold salts in the solution of PMPP in solution forms stabilized gold nanoparticles. The ratio of gold salt to PMPP allows some control over the size of the synthesized nanoparticles. Termination of a percentage of methyl groups of PMPP with thiol allows further stabilization and preservation of gold nanoparticles. The introduction of carboxylic acid side groups provides regions of hydrophilic character on the polymer, giving rise to hydrophilic/hydrophobic interactions to order the nanoparticles into specific domains. Grafts and block copolymers of PMPP with conventional organic polymers are used to stabilize gold nanoparticles at localized domains of PMPP. Solutions of PMPP / gold nanoparticles, and PMPP derivatives with gold nanoparticles are studied with optical spectroscopy, and microscopy. Films of the PMPP / nanoparticle composites are characterized by optical spectroscopy and microscopy to determine conditions which promote growth of the nanoparticles and stabilization to form short wires and non-spherical aggregates within the localized domains.

C4.17 **CHARACTERIZATION OF ANISOTROPIC NANOPIRICLE MATERIALS USING SMALL-ANGLE SCATTERING.** John D. Bell, National Polymer Characterization Group, Gaithersburg, MD.

Small-angle scattering methods using both x-rays and neutrons are well established for characterizing the morphology of materials on nanometer distance scales. This presentation provides a general overview of these methods as they have been traditionally used to characterize materials ranging from virus particles to microphotontronic structures. More recent research studies on materials whose anisotropy is due to anisometric particles in assemblies with preferred orientation will be described to illustrate the general principles used to elucidate such morphologies.

C4.18 **FABRICATION OF AMPHILIC GOLD NANOPARTICLES.** Joseph M. Simard, Cheryl L. Briggs, Andrew K. Boal, Vincent Rotello, University of Massachusetts at Amherst, Dept. of Chemistry, Amherst, MA.

Mixed monolayer-protected gold clusters (MPGCs) provide versatile precursors for the fabrication of nanoparticles. One potentially powerful application of MPGCs is a biomolecular recognition: in recent investigations we have demonstrated that the mobility of thiolate ligands on nanoparticles can be exploited to create templated micromotors. In this methodology, the recognition of protein surfaces, however, has been limited by the insusceptibility of water-soluble amphiphilic MPGCs. To provide these essential systems, we have explored the exchange of polar functionality into gold nanoparticles featuring nonpolar monolayer coverage. We report here the direct formation of water-soluble amphiphilic colloids through phase exchange of solubilizing groups including alkylmethanethiols with thiol carboxylic acid. The fabrication and properties of these systems will be discussed.

C4.19 **EFFECT OF CHAIN LENGTH ON INTRA-MONOLAYER NONCOVALENT INTERACTIONS IN SAMS ON GOLD NAPARTICLES.** Andrew K. Boal, Vincent Rotello, University of Massachusetts at Amherst, Amherst, MA.

Unlike the highly ordered self-assembled monolayers (SAMs) formed on flat gold surfaces, those on gold nanoparticles radially form a roughly spherical center and are amorphous in structure. One result of this structural motif is the strength of intermonolayer non-covalent interactions, such as hydrogen bonding, are a function of the distance of the recognition element from the colloidal core. We present here an exploration of these phenomena in a number of systems, and present some fundamental rules for incorporating intermonolayer noncovalent interactions in the design of new SAM-nanoparticle systems.

C4.20 **PLANAR SYNTHESIS OF OBLATE NAPARTICLES.** Gadneya B. Khomotso, Yury A. Kokashov, Alexander Yu. Obidenov, Eugeny S. Saldinov, Artem S. Trifonov, Faculty of Physics, M.V. Lomonosov Moscow State Univ, Moscow, RUSSIA; Sergey P. Gubin, Institute of General and Inorganic Chemistry RAS, RUSSIA.

The control of matter on the nanometer-length scale and nanoparticles research are the key components of nanoscience nanotechnology. Shape and size control of nanoparticles is important for practical applications. The method of nanoparticles synthesis often influences the properties of the product, particularly the shape, size, morphology and degree of crystallinity. A novel method of two-dimensional synthesis of nanoparticle colloids was introduced recently [1]. In this method oblate nanoparticles are fabricated via decomposition of a volatile organic solvent. Metal precursor compound in a mixed surfactant monolayer at the gas/liquid interface, and nanoparticles growth is an example of two-dimensional process where surfactants, precursors, intermediates, nucleus and nanoparticles form a monolayer at the interface. In our experiments nanoparticles were generated by ultraviolet decomposition of iron pentacarbonyl, diiodo octacarbonyl and by chemical reduction of metalorganic cluster molecules in a mixed monolayer with stearic acid on the water surface. The properties of nanoparticles are dependent on the length of about nanometers to hundreds of microns with thickness about 1-8 nm. X-rays scattering in the low angle range revealed several Bragg reflections indicating layered structure of ultrathin nanoparticles in multilayer particular Langmuir-Blodgett films formed in agreement with scanning probe microscopy measurements. TEM data point out to the amorphous structure of nanoparticles. Two-dimensional monolayer nanoparticle synthesis provides ultrathin nanoparticles with very high surface to volume ratio, what is a perspective for catalysis, optical and other applications. [1] G.B. Khomotso et al. MRS. Sci. Eng., C, 8-3 (1999) 269-278.
C4.21 SYNTHESIS AND CHARACTERIZATION OF POLY- (2-PROPIONYLCHLORIDE)/ACRYLIC ACID COPOLYMER FILAMENTS. William D. Holliday, L. Andrew Lyon, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA.

We report the preparation of environmentally responsive, rod shaped hydrogel nanoparticles via template-directed synthesis. Poly(N-acryloylchloride)/acrylic acid copolymer matrices (both monolithic and spherical particles) have been shown to reversibly swell in response to a temperature change in the surrounding environment.

Temperature phase transitions were studied on this system and compared to literature values of monolith systems and sub-micron spherical particles of similarly composed hydrogels. Characterization of particle size, shape, and responsivity was carried out using optical and confocal microscopes.

C4.22 PHOTOMECHANICAL RESPONSE OF AZOBENZENE / FLUOR-MICA COMPLEXES I: ORGANOPHILIC MICA AS HOST. Takeo S. Fujita, N. Iyida, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN; Zenon Kupryja, Faculty of Geology, Geophysics and Environmental Protection, University of Mining and Metallurgy, Krakow, POLAND.

The photomechanical properties of organophilic fluoro-catenaric micaceous (o-TSM) / azobenzene complexes were investigated to reveal optimum conditions for large photomechanical response. The alkyl chain length and the concentration of trimethyl-aluminium (TMAH) were varied to prepare 16 o-TSM hosts. These were classified as having either bimolecular, pseudo-trimolecular or paraffin type structure based on judgments of basal spacings. Azobenzene-o-TSM complexes were prepared by vacuum phase intercalation of azobenzene (AzBu) into o-TSM and were characterized by CHN analyses and XRD measurements. Photomechanical responses for the complexes were monitored by changes in d(001) under UV irradiation (λ = 365 nm). A large photoreponse, indicated by a 0.25 - 0.5nm decrease in d(001), was observed for the complexes with o-TSM hosts classified as having a pseudo-trimolecular structure with basal spacing of 2.2 - 2.5 nm. The increase in the basal spacing of these hosts due to AzBu incorporation was 1.2 - 1.4 nm, which is almost equal to the long-axis length of AzBu, suggesting a vertical arrangement of AzBu within the layer. For the complexes which little or no photoresponsiveness, the basal spacing of the o-TSM hosts were either less than 2.0 nm or about 3.9 nm, which were classified as having bimolecular and paraffin-type structures respectively. These results indicate that the photoreponses is closely related to the structure of the o-TSM hosts for these complexes, and that pseudo-trimolecular structure o-TSM hosts can provide complexes with good photoreponsive properties. The photo-mechanical properties of the organophilic micaceous complexes with organophilic macromolecules (o-TNM) would be presented.

C4.23 Abstract Withdrawn.

C4.24 POLYMERIC SURFACANTS BASED ON OLEIC ACID. Qingfang Fu, Institute of Materials Science, University of Connecticut, Storrs, CT.

The lamellar liquid crystalline (LLC) region in the system consisting of sodium oleate [NaO1], oleic acid (OLA), and water was determined. The interlayer spacings (d) of the lamellar liquid crystals were measured and extrapolated to zero water content to obtain dl0 values. The dl0 values showed the oleic acid to be solubilized between the methyl group layers at low concentrations and interdigitating between the hydrocarbon chains for greater contents. Cross-linking agents were added to the system. They were found located partly between the end methyl group layers and partly interdigitating between the hydrocarbon chains. The LLC phase of NaO1/OLA/H2O system with the cross-linking agent was polymerized. The system after polymerization was a mixture of LLC phase and solid. The order of the arrangement in LLC phase, but also in the hydrophobic layer between the methyl groups. The polymer lowered the surface tension of water to below 30mN/m with a CMC of 0.25g/L.

C4.25 FABRICATION AND CHARACTERIZATION OF CHROMIUM OXIDE NANOPARTICLES. Zhiwen Zhou, Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA; Department of Physics, Grambling State University, Grambling, LA.

Well-dispersed nanoscale textured chromium oxide particles can be fabricated under certain conditions by laser-induced solution deposition (LISD) from organic solvents. The fabricated nanoparticles are characterized by scanning electron microscope with EDX, transmission electron microscope, X-ray diffraction and magnetic measurements. We have successfully demonstrated that the LISD is a unique technique for fabricating uniformly-distributed but anisotropic chromium oxide particles, which can be used in electronic/magnetic devices.

C4.26 HIGH COERCIVITY IN NANO-CRYSTALLINE FERRITE MATERIALS. Yu Shi, Jun Ding, National University of Singapore, Department of Materials Science, SINGAPORE.

In this work, nanocrystalline barium and cobalt ferrites were prepared by mechanical milling and sputtering. It has been found that the coercivity of these compounds could be dramatically enhanced by adopting nanomagnetic elements. The magnetic properties are strongly dependent on the concentration of nanomagnetic elements (alumina and silica, respectively) and heat treatment condition (annealing temperature and duration). A coercivity as high as 93 kOe was obtained in Al substituted bar ferrite, while the coercivity values of the Bi-ferrite samples without doped Bi with a similar particle size were in the range of 5-6 kOe. Cobalt ferrite/silica nanocomposite with a coercivity of 3.3 kOe and a magnetization of 57 emu/g was obtained. The sputtered Co ferrite/silica nanocomposite possessed a coercivity as high as 7.5 kOe, which is the highest value for Co ferrite according to our knowledge. The structure and magnetic behavior of these nanocrystalline specimens were investigated by X-ray diffraction, Mossbauer spectroscopy, Transmission electron microscope, Scanning electron microscope and Vibrating sample magnetometry.

C4.27 VOLUME CONFINED STATES IN ELLIPSOIDAL QUANTUM DOTS. Giovanni Castello, Domenico Ninno and Giuseppe Iadonisi, Istituto Nazionale di Fisica della Materia (UdR Napoli) and Univ. di Napoli Federico II, Dipartimento di Scienze Fisiche.

The Shr"{o}dinger equation has been solved, within the effective mass approximation and using hard walls boundary conditions, in an ellipsoidal quantum dot (QD) with anisotropic symmetry for studying the role of the QD shape on the system's physical properties. An exact numerical solution allowing the calculation of all the spectrum has been obtained using a suitable coordinate system in which the wave function is separable. The variable separation leads to a one-dimensional Schr"{o}dinger equation which has been solved numerically with a midpoint shooting algorithm. Our main result is that it is not enough to specify the system dimensions and volume in order to determine the energy spectrum. We have indeed, shown that if one considers a family of ellipsoidal QDs with constant volume, the ground state energy depends on the anisotropy degree (the ratio a/c between the major and minor semi-axes) of the structure. Looking at the ground state energies as a function of a/c (keeping the volume constant) it is found that minimum is reached for the spherical QD. We have also considered excited states and found that the ellipsoidal deformation determines both a splitting of the states with different z-component of the angular momentum, and a volume effect similar to that found for the ground state. The system geometry plays a very important role also in determining the wave function angular dependence. We have found, in particular, that while in the spherical QD the ground state wave function does not depend on the angular coordinates (reflecting the full rotational symmetry of the system), for ellipsoidal QDs it presents a localization in the points corresponding to the ellipsoid section passing for its centre and orthogonal to the major axis. Finally, surface dielectric effects due to the dielectric constant difference between the dot and the surrounding medium are discussed.

C4.28 DEPOSITION OF AN EXTREMELY THIN POLYMER FILM ON CERAMIC nanoparticles. Dongshu Shi, Wai van Ooij, Jiangang Zhao, and Zhou Yu, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH; Xianbi Wang and Lumin Wang, Dept. of Nuclear Engineering and Radiological Science, University of Michigan, Ann Arbor, MI.

To achieve unique properties in fundamental research and cutting edge technology there is a critical need to develop structures on nanoparticle surfaces. Such a structure has to be at nano-scale so that it can be a substructure of the nanoparticle. This implies that the surface of a nanoparticle is tailored only at a few nanometers in terms of structure, composition, and uniformity. The great challenge therefore lies critically on the deposition of a film on the order of a few nanometers on the surfaces of the nanoparticles. Here we demonstrate, for the first time, the uniform deposition of ultrathin films of 2 nm on the surfaces of alumina nanoparticles using a plasma
C4.20 SYNTHESIS AND CHARACTERIZATION OF NONSCHERICAL COLLOIDAL PARTICLES WITH UNIFORM AND WELL-CONTROLLED SIZES AND SHAPES, Yu Lu, Yuding Yin, Yoann Xiu, Univ of Washington, Dept of Chemistry, Seattle, WA.

We have recently demonstrated several effective methods for generating monodispersed, nonspherical colloidal particles with well-defined dimensions and shapes. Typical examples include ellipsoidal polymersomes, parametrically shaped polymer beads, and dumbbell-shaped capsules. In this presentation, we will outline the detailed procedures, as well as the unique features and applications of these nonspherical colloidal particles.

C4.30 TRANSPORT PROPERTIES OF BI-RELATED NANOWHIE, ARILAY, Y., Min Li*, S.B. Cronin, O. Rubin, J. Heremans, M.S. Dresselhaus*, J.Y. Ying*, "Department of Electrical Engineering and Computer Science, Department of Physics, Department of Chemistry, and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA; Delphi Automotive Systems, Warren, MI.

Due to their reduced dimensionality and enhanced surface/volume ratio, one-dimensional nanowires exhibit unusual physical properties and have great potential for application in novel optical, electrical, magnetic, and terahertz electronic devices. Nanowires have been exploited extensively for the synthesis of large-scale self-assembled nanowire arrays for a variety of materials using pressure injection, electrochemical deposition or vapor deposition techniques, resulting in monodimensional and nanoassembled nanowire arrays. In this paper, biasmith (Bi), antimony (Sb) and Bi-Sb alloyed nanowires with wire diameters ranging from 200 nm down to 10 nm are fabricated in porous silicon nanowires by pressure injection or vapor deposition techniques. The nanowire arrays are characterized by SEM and X-ray diffraction to determine the crystal structure, and transport measurements of these nanowire arrays are performed. Bi, as a semimetallic Group V element, is a promising candidate for the study of quantum confinement effects at larger, easily accessible sizes because of the very small electron effective masses in Bi. In addition, it is expected that the band structure of Bi nanowires can be controllably engineered by alloying Bi with antimony (Sb) to produce an enhanced thermoelectric efficiency. A theoretical calculation for the band structures of these nanowires is developed, which predicts a semimetal-semiconductor transition for Bi and Sb nanowires at wire diameters of 50 and 9 nm, respectively. Based on these calculations, a semi-classical transport model for nanowires has been developed and compared with experimental results.


C4.31 TAILORING GRAPHITE SHEETS TOWARDS MESOSCOPIC DEVICES, Erik Di Grandi, Tineke Thio, NERC Research Institute, Princeton, NJ; Henri Lezoec, Thomas W. Ebbesen, ISIS, Louis Pasteur University, Strasbourg, FRANCE.

For a number of reasons, graphite can be considered as a frontier material between the solid state and the molecular worlds. Hence, in the recent years, both condensed matter physicists and chemists have united their respective band structures of graphite in a variety of its morphologies: fullerines, nanotubes, cones, etc. For theorists, the ideal graphic object is the graphene sheet, which is a single layer of plane graphite. The very unusual transport properties of graphene, when constrained in its lateral dimensions, have been widely studied theoretically [1]. For instance, it has been shown that the danging bonds (unpaired electrons) of one edge of a narrow band of graphene would be ferromagnetically coupled [1]. To the best of our knowledge, neither the magnetic ribbons of graphene have been observed [2], nor experimental data on properties of small contractions of graphene have been made available. We will present our experimental results on 70 nm wide contractions in graphite nanofibers of the name nanofibered Focused Ion Beam lithography (FIB). In our samples, both the mesoscopic constuction and the terminal electrodes are cut in isolated graphic sheets having a diameter of 1 to 2 microns and a thickness of about 100 bond planes. The preparation of the samples along with the advantages of our approach will be discussed.

The magneto-transport properties of the contractions have been characterized and evidence of size effect on the electronic properties of graphene have been identified. Our experiments are the first of its kind [3]. Perspectives of our promising results toward the experimental study of mesoscopic graphene and its outstanding challenges will be discussed.


Arrays of 10 to 120 nm diameter single crystal bismuth nanowires have been formed inside amorphous aluminum templates. Since bismuth has a small effective mass compared to other materials, significant quantum mechanical confinement is expected to occur in wires with diameters less than 50 nm. The subbands formed by quantum confinement cause interesting modifications to dielectric function of bismuth. This study measures the dielectric function of bismuth nanowires in an energy range where the effects of quantum confinement are predicted (0.08 to 0.5 eV). Using Fourier transform infrared reflectometry, the dielectric constant as a function of energy is obtained for the alumin/bismuth composite system. Effective medium theory is used to subtract the effect of the alumina template from the measurement of the composite material, thus yielding the dielectric function of bismuth nanowires. Several oscillators are observed in the frequency dependent dielectric function in the photon energy range measured. The dependence of the frequency and intensity of these oscillators on doping, polaronization, and diameter of the nanowires will be reported. We gratefully acknowledge the support of MURI subcontract 0295-G-7A114-01, NSF grant DMR-88-04724, and the US Navy contract N00172-88-K-0024.

C4.33 SURFACE ELECTRICAL TRANSPORT AND LONG RANGE ELECTROSTATIC TRAPPING OF DNA MOLECULES, V. Sumukho, Y.S. Lee, D. Gersappe, J. Sokolov, M. Rashsubikh, Dept. of Materials Science, SUNY at Stony Brook, NY; N. Peredet, Dept. of Biology, SUNY at Stony Brook, NY; B. Chu, Dept. of Chemistry, SUNY at Stony Brook, NY.

The electrical transport properties of long DNA molecules were studied based on a newly developed method of electrophoresis on flat surfaces [1]. The electrostatic properties of DNA in the presence of Si surface were found to be approximately one order less than in free solution. The dielectrophoresis peaks of 1 kb- and Hind III DNA ladder have been clearly identified. The experimental dependences of the molecular on molecule (MOM) DNA molecules were found to be well fitted to a power law with the exponents of an opposite sign to different buffer concentrations: negative for surface transport at 10^-7 M M concentration of TBE buffer and positive at 10^-5 M. A novel mechanism responsible for DNA molecules separation at the presence of the surface at low buffer concentrations has been developed. The long-range electrostatic trapping [2,3] creates molecules weight distribution of DNA within the electric double layer in normal to the surface direction. The electric double layer is responsible for the velocity profile of the electroacoustic flow. The net electrophoretic mobility of longer DNA, being trapped closer to the surface, is higher than of the shorter ones in the electric field, oriented along the surface. The main features of the electrohydrodynamic instability [4] related to Λ and T₂ DNA molecules aggregates, observed in our system, are consistent with the concept of long-range electrostatic trapping. This work was supported by NSF-MRSEC Program, 1. N. Peredet et al., submitted to J. Am. Rev. Lett. 2. X-HN, et al., Science, 1995 3. A. Lisen et al. Nature, 385, 239 (1997) 4. L. Mitnik et al., Science, 267, 229 (1995).

C4.34 CONTROL SYNTHESIS OF HIGHLY LUMINESCENT CdSe AND CdSe/ZnS QUANTUM DOTS, Weng Hao, Moungi Bawendi, MIT, Dept of Chemistry, Cambridge, MA.

Physical properties and potential applications of CdSe quantum dots (QDs) have been extensively explored in the last decade. CdSe QDs with high photoluminescence (PL) quantum efficiency (QE) not only increase the sensibility of experiments, but also make their potential applications more promising. We report here a simple but powerful recipe to improve the QE of CdSe QDs and core-shell (CdSe/ZnS) QDs. The QE of these treated QDs is increased by up to an order of magnitude from untreated values. Subsequent coating of CdSe QDs with ZnS reproducibly yields composites with QE as high as...
C4.35
PHOTOELECTRICITY OF CHARGED CdSe QUANTUM DOTS.
Wing Woo, Ken Shimizu, Robert G. Neusen, Catherine A. Loeberdahl, Meng G. Bawendi, MIT, Dept. of Chemistry, Cambridge, MA; Michael P. Rumsey, MIT, Dept. of Materials Science and Engineering, Cambridge, MA.

A charged quantum dot (QD) is believed to be thirker than the direct charge quenches the photocurrent (PL) through non-radiative Auger processes. This model has been applied to explain both photodarkening effects observed in QD glasses and PL intermittency observed in single QDs. However, direct experimental proof has been lacking. We discuss here results that show electrical injection of carriers into a QD results in a very efficient, smooth diamond films deposited by HFCVD method. The seeding technique has improved the addition of diamond films and helps to grow high quality textured diamond films. The detailed investigations to grow high-quality diamond films will be discussed in this paper. This research was supported by Alabama NASA-EPSCoR program.

C4.36

Because transport in nanowires is confined to one dimension, nanowire properties are particularly sensitive to even slight variations in structure and composition, as well as wire diameter. The properties of nanowire arrays, composite materials that result from the interplay of electronic, phononic, and information storage, for example, are strongly dependent on the structure and composition of not only the nanowires but also the wire-string interfaces. In this work, we have employed transmission electron microscopy (TEM) and analytical electron microscopy to assess the structure, composition, and electronic properties of arrays of bismuth and bismuth telluride nanowires at high spatial resolution. The wires were fabricated by pressure injection (Bi) or electro- deposition (Bi$_2$Te$_x$) into porous molybdenum alumina templates. Using imaging and diffraction in the TEM, we have found that the wires are polycrystalline with varying grain sizes depending on the processing conditions. Energy dispersive x-ray spectroscopy has been employed to assess the local composition of the wires. The bismuth telluride wires are constant in composition except in a localized region at the wire edge, which is Tellurium-rich due to the deposition mechanism. Finally, the local electronic properties of the bismuth nanowire arrays have been assessed using electron energy loss spectroscopy in conjunction with energy-filtered imaging. We have found that the bismuth volume plasma peaks vary in energy and width as a function of wire diameter, due to quantum confinement and surface effects, and a localized plasma present at the bismuth-alumina interface.

C4.37
CRYSTALLOGRAPHIC DESCRIPTIONS FOR NANOPARTICLE ASSEMBLIES - APPLICATION TO SELF-ASSEMBLED SIZE-SELECTED CADMIUM Selenide CLUSTERS. Alexandre V. Vasilev, Mark Anzana, Dept. of Metallurgy and Materials Engineering, University of California, Berkeley, Photos Papadimitrioukopoulos, Dept. of Chemistry, University of Connecticut, Storrs, CT; Enquir Jain, Dept. of Electrical and Computer Engineering, University of Connecticut, Storrs, CT.

Self-assembled semi-modal sized-selected nanoparticles frequently adopt close-packed three-dimensional arrangements. The resemblance of these arrangements to the face-centered cubic or hexagonal close-packed crystal structures exhibited by many of these materials has led to the widespread adoption of these crystallographic terms to describe the assemblies. More recently, it has been shown that well-ordered non-close-packed assemblies of both semiconductors and bimodal sized-selected clusters can be produced. Such arrangements can also be described crystallographically as the analogues of structures exhibited by binary alloys and compounds. In this paper, we will present the different structure types which can be exhibited and the changes which will be illustrated using two transmission electron microscopy data obtained from assemblies of CdSe nanoparticles produced by solvation pyrolysis of organometallic precursors in tricyclohexylphosphine oxide. The effects of surface states and the ratio of particle diameter to bimodal size distributions on the structure adopted will be discussed. It is shown that such descriptions provide not only a convenient notation for the arrangement exhibited in a particular assembly, but also a framework for describing interferences of CdSe nanoparticles which can influence collective properties as crystal defects.

C4.38
GROWTH OF HIGHLY TEXTURED DIAMOND FILMS ON Si (100) SUBSTRATES BY NANO-PARTICLE SEEDING.
TECHNIQUE. Ashok Kumar, Department of Electrical and Computer Engineering, University of South Alabama, Mobile, AL.

Nanocrystals powders, with particle size in the 1-10 nm range, have shown great promise in the forming of advanced structural and functional materials for applications in tribological coatings, high surface area catalyst support for thermal catalyzer, and capacitor and battery materials, dielectric and optoelectronic materials. CO2 laser deposition of ceramic powders from gas-phase precursors is an ideal method for growing thin films, which has resulted high quality smooth diamond films deposited by HFCVD method. The seeding technique has improved the addition of diamond films and helps to grow high quality textured diamond films. The detailed investigations to grow high quality diamond films will be discussed in this paper.

C4.39
SHEET ORIENTATION OF VISCOELASTIC POLYMER-CLAY SOLUTIONS. Gafur Schmid, Alan I. Nkrumah, Peter Bayer, Alumgir Karim, Charles C. Hsin, NMST.

The influence of shear on viscoelastic clay-polymer solutions was investigated by means of rheology, flow birefringence and small-angle neutron scattering (SANS). Oscillatory shear showed that linear viscoelastic behavior occurred when a critical strain was reached. With increasing steady shear rate a pronounced minimum in birefringence was observed at a critical shear rate corresponding to the orientation of the polymer-clay system. The polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. The degree of orientation could be achieved by either constant strain rate or constant stress experiments. SANS measured the shear-induced orientation of polymer and platelets as a function of shear rate. At rest and at low shear rates a diffusive isotropic ring of scattering intensity was observed. With increasing shear rate an anisotropic scattering pattern developed. At higher shear rates, the scattering minorty increases due to the increased orientation of the clay platelets in the shear field. The results lends to fast recovery demonstrating the system to be highly elastic.

C4.40
OPTICAL RESPONSE OF GOLD NANOCRYSTALS IN DIELECTRIC MATERIALS. S. Akira Ueda, Elena M. Bryant, Carlton B. Maxwel, Charlene M. Blake, Richard R. Mu, Marvin H. Wu, Andrej I. Zawadzki, and Donald G. Henderson, Chemical Physics Laboratory, Department of Physics, Fisk University, Nashville, TN.

Surface plasma resonance (SPR) of mesoscopic metal particles has been extensively studied in the past. Besides the many potential applications, there still have been fundamental interest and questions of such small metal particles. We have fabricated nano-sized metal particles in/on some transparent substrates by using several methods such as ion implantation, pulsed laser deposition, and electron beam evaporation. Previously we have reported that the atmosphere affects the position of SPR in the system of MgO implanted with Au [1]. In addition to this study, recently, by using the pulsed laser deposition method, gold nanocrystals were formed on several substrates, and the gold deposited samples were coated with some insulating materials by the α-emission evaporation method to investigate the surrounding material dependence of SPR band of gold particles [2]. A. J. Ueda et. al, Nucl. Instr. and Methods in Phys. Res. B 141 (1998) 261-267.

C4.41
AMINE BASED LAYER BY LAYER GROWTH OF SEMICONDUCTOR NANOCRYSTALS FOR EL APPLICATIONS. Jeonghoon Lee and Photos Papadimitrioukopoulos, Nanomaterials Optoelectronics Laboratory (NOEL), Polymer Program, Department of Chemistry, University of Connecticut, Storrs, CT; Craig Jain, Nanomaterials Optoelectronics Laboratory (NOEL), Department of Electrical and Systems Engineering, University of Connecticut, Storrs, CT.

Building a precisely controlled assembly is essential for application of semiconductor nanocrystals in optoelectronic devices such as light emitting diodes (LEDs). CdSe nanocrystals were synthesized by pyrolysis of organometallic precursors. Dimethylcadmium and selenium were used for the growth of CdSe nanocrystals. Solvent tricyclophosphine (TOP) Diethyl zinc and hexamethyl-
composites allows the creation of structured materials, with interesting electronic, optical, optoelectronic, and magnetic properties. In recent research, we have developed a "building block" approach to electrostatically mediated construction of modular self-assembled colloidal-building assemblies. Our strategy involves functionalization of one type of colloidal building block with a primary amine, and a counterpart building block with a carboxylic acid derivative. By combining the two systems, acid-base chemistry followed by immediate charge-pairing resulted in the spontaneous formation of electrostatically bound mixed-colloid constructs. The shape and size of these assemblies were controlled via variation of particle size for the two components and their stoichiometries.

**C4.47 CONVENTIONAL MOLECULAR APPROACH OF SIZE AND SHAPE CONTROLLED ZnSe AND ZnTe NANOCRYSTALS**

By J. Park, J. Cheon, Department of Chemistry and School of Molecular Science-BK21, Korea Advanced Institute of Science and Technology (KAIST), Taejon, KOREA

We describe a convenient one-step synthesis of ZnSe and ZnTe nanocrystals (NCs) whose sizes and shapes are precisely tuned by the growth temperature or growth time. We utilized molecular precursors; bis(phenylethynyl) or telchelic:p-n,N,N'-tetramethylethylendiamine (TMEDA), which effectively produce 0-dimensional spheres or 1-dimensional nanorods of ZnSe and ZnTe. Nanocrystals are highly monodispersed and luminescent; the emission wavelength varies over a wide range depending on the particle size. This study constitutes a nice demonstration of direct size and shape controlled synthesis of semiconductor NCs and this method can be extended to the synthesis of nanocrystals of other materials.
To confer upon rechargeable lithium batteries the capability of delivering very high currents, nanocomposite electrodes have been designed, synthesized, and tested. Anodes comprising carbon nanotubes connected to a dispersion of metal nanoparticles, all self-assembled within a block copolymer acting as template, have been characterized in coin-cell battery test configurations. The same is true for cathodes comprising carbon nanotubes coated with vanadium oxide self-assembled with a block copolymer. In charge/discharge tests over hundreds of cycles at rates as high as 4 C, these electrodes exhibited high resistance to capacity fade.

**Abstract Withdrawn.**

**10:15 AM C5.5 ELECTROCHEMICAL PATHWAYS TO NANYRES AND NANTUBES.** Martin Moskovits, Konstantin Shelimov, Anita Oslin, Diyan Abassov, Dimitri Troytak, Jody Young, University of Toronto, Chemistry Department, Toronto, CANADA.

Highly regular periodic arrays of pores can be fabricated by electrochemical etching of cathode films. The dimensions of the pores can be controlled almost continuously with pore diameters ranging from 10-140 nm, pore lengths from 0.5 to over 100 μm, and pore densities from 10 to 10^3 cm^-2. These porous films can then be used as templates from which to cast metal or semiconducting nanowires or nanotubes by judicious use of electroplating or chemical vapor deposition or as contact masks for nanoscale lithography or etching. In this manner, we have successfully generated carbon and boron nitride nanotubes, layered nanotubes that act as arrays of nanocapacitors, nanoscale tunnel junction devices that display room-temperature Coulomb blockade effects and field-emission cathodes. Electrical measurements on single nanowires as well as on nanowire arrays have been carried out using SEM as a single wire probe.

**10:45 AM C5.6 ANISOTROPIC NANOMECHANICS OF BORON NITRIDE NANOCONDUCTORS.** S. S. P. Parkin, University of Colorado at Boulder, Institute of Materials, Cambridge, MA.

Investigation of mechanical properties of boron nitride nanotubes using a general thin-film testing method reveals many interesting nanoscopic characteristics that can be directly attributed to band bending effects. In particular, we have observed a novel anisotropic strain-release plastic buckling in which tubes plastically buckle on one end when axially compressed from both ends. Based on the results of these tests, skin in zigzag BN nanotube-reinforced composites is proposed which will have distinct anisotropic characteristics against external compression and tensile deformations.

**11:00 AM C5.7 4-POINT RESISTANCE MEASUREMENTS OF INDIVIDUAL BINAWS.** S. B. Cronin, Y. M. Lin, J. Heremans, M. S. Dresselhaus, Department of Physics and Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA.

4-point measurements are made on individual Bi nanowires with diameters ≤ 200 nm. The nanowires are fabricated using a self-assembly, non-lithographic technique by filling modified alumina templates with molten Bi. [Wires of PbTe and Bi₂Te₅ prepared in the same aluminum templates will also be discussed.] The 4-point contacts are affixed to the nanowires using an electron beam lithography technique. Measurements are made as a function of temperature and magnetic field for a variety of wire diameters in the range from 40 to 200μm. The theoretically predicted semimetal-semiconductor transition due to the shifting of band edges arising from the quantum confinement of electrons is observed. The resistance versus temperature R(T) results are explained by considering the predicted band shifts due to quantum confinement and the effects of various scattering mechanisms. The role of wire boundary scattering, which is found to be particularly important in the Bi nanowires relative to bulk Bi, is discussed. We gratefully acknowledge the support of MRSEC subcontract 45985-G-ZA114-14. NSF grant DMR-9634254, and the US Navy contract N00167-98-K-0924.
1:30 PM **C6.1**  
**NANOBIOTECHNOLOGY-BASED DETECTION METHODS FOR DNA**  
Chad A. Melsen, Andrew Bacon, Northwestern University, Chemistry Department, Evanston, IL, Robert Letsinger, Nanostructure, Inc, Willimette, IL.  

Nanostructure-based methods for detecting DNA will be described. These methods, which are based upon metallic and semiconductor quantum dot materials, offer significant advantages over conventional methods with regard to speed, selectivity, sensitivity, and ease of use. The origins of these advantages and their technological implications will be discussed.

2:00 PM **C6.2**  
**DNA-DIRECTED ASSEMBLY OF ANISOTROPIC NANOBEADS ALONG CUBIC ELECTRIC FIELD LINES**  
Paul B. Weiss, Brian R. Deady, Northwestern University, University Park, PA.

Recently there has been a great deal of interest in DNA as a “smart glue” for assembling two-dimensional structures in inorganic building blocks. To date, most of this work has focused on isotropic nanostructures, but anisotropic nanostructures possess the ability to assemble more complex nanoscale structures. In this work, anisotropic noble metal nanoparticles have been synthesized and assembled using a template synthesis strategy. The particles have been released from the template to form cubic rods of anisotropic nanoparticles. These nanoparticles have been modified with DNA oligomers of varying length using several different attachment chemistries and then the technique of modifying these particles with DNA has been explored, and the DNA has been used to assemble the particles at planar Au surfaces as well as lithographically defined Au pads on Si wafers.

2:15 PM **C6.3**  
**NANOSPHERE LITHOGRAPHY. SYNTHESIS OF NANOSPHERICAL METALLIC NANOBEADS AND APPLICATIONS IN SURFACE CHEMISTRY**  
Chun L. Haynes, Amanda J. Hesse, Michelle D'Alma, Daniel M. VanOoyen, Northwestern University, Dept. of Chemistry, Evanston, IL.

Early work with size-tunable periodic particle arrays (PPAs) fabricated by nanosphere lithography (NSL) demonstrated that the localized surface plasmon resonance (LSPR) could be tuned throughout the visible region of the spectrum. The LSPR is sensitive to changes in nanoparticle aspect ratio and local dielectric environment. Single layer PPAs consist of size-tunable anisotropic nanoparticles that can be modified to exhibit anisotropic surface plasmon resonance (SPR). This work demonstrates multiple schemes for PPA modification using self-assembled monolayers and colloidal decoration. Nanoparticle anisotropy can be further exploited with the recent combination of NSL and reactive ion etching (RIE); this extends the two-dimensional PPA structure into the third dimension. The LSPR of nanoparticle colloids can be modulated and tuned in the same fashion as the two-dimensional arrays. This, as well as the added control of the nanoparticle dielectric environment, generates a new class of PPA-based nanostructures. Potentially useful new nanostructures include encapsulated PPAs, high aspect ratio nanorods, and electromagnetically-coupled stacked nanoparticles.

2:30 PM **C6.4**  
**OPTICAL CHARACTERISTICS OF CdTe QUANTUM DOTS IN BIOLOGICAL APPLICATIONS**  
William Meiklejohn, Stephen Emperdocks, Jin Jin, Joseph Treadway, Marcel Bruchez, Steven Ung, Edward Adams, Quantum Dot Corporation, Palo Alto, CA.

Semiconductor nanocrystals have generated considerable interest as biological labels. Their unique combination of properties, such as high luminescence, photostability, broad excitation spectra, narrow emission spectra and long fluorescence lifetimes, provide for an extremely versatile fluorophore with the potential to outperform existing biological markers. Characterization of quantum dots within biological milieu is essential so that the preparation and detection of these nanoparticles are optimized for performance as biological markers. Thus, how quantum dot properties evolve due to environmental changes inherent in biological applications, such as surface modification, solvation by water, bioconjugation and binding to an array of surfaces, must be understood and controlled. This presentation will describe several unique characteristics of CdTe/ZnS core/shell quantum dots, methods of measurement and how they can be exploited in biological detection systems.
which the certain crystal relation between orthorhombic \cite{110} of NiCo and cubic \cite{311} of Ni2Co, face-center crystal \cite{222} of NiO, cubic \cite{111} of nickel have been identified and confirm the nature of this core-shell nanocomposite particles. It is evident that this is an interesting magnetic nanomaterial stemmed from the nature of core-shell of microstructure.

Magnetization measurements of these particles assemblies have been performed using a SQUID magnetometer at different applied fields and low temperature. It is suggested, this nanocomposite particles assemblies display superparamagnetic behavior above a wide range before blocking temperatures (T blocked) of 190K, this superparamagnetic relaxation behavior is found to be modified by interparticle interactions, which depending on the applied field, size distribution; the surface magnetocrystalline anisotropy induced from exchange interaction with random anisotropy among particles assemblies. On the other hand, antiferromagnetic order occurs with a Neel temperature (T Neel) of about 11K. A spin-flip transition is also observed below T_N at a certain applied field. In particular, the exchange coupling interaction between pure NiO and core-shell NiO core/shell systems are responsible for their higher coercity (H_c). Furthermore, the EPR spectra at low and room temperature reflect these magnetic order associated with the core of core-shell nanocomposite crystallographic character anisotropy and size distribution, coupling with the strong interparticle interaction.

4:30 PM C7.6
SYNTHESIS OF BRUSH-LIKE CONDUCTING POLYMER NANOPARTICLES AND THEIR EFFECT ON MEDIATING LI+ TRANSPORT FROM LIQUID ELECTROLYTES TO CATHODE
Yong Poon, Ning Yang, Ling-Ling, Hong Kong University of Science and Technology, Dept of Chemical & Environmental Engineering, SINGAPORE

A new approach to the synthesis of nanoscale particles of polyprrole (PPy) and polyaniline (PANI) is presented. By this method, several kinds of core particles of polyacrylate (POE) and polyaniline (PANI) with their polaron moiety were chemically grafted to polyprrole and aniline molecules through tetraylene disocyanate (TDI). The modified polyprrole or aniline molecules, together with unmodified counter parts, were subsequently subjected to chemical polymerization in a THF / water mixture, which resulted in very stable colloidal dispersions. The particles obtained should possess brush-like architectures in the dispersing medium, and their TEM sizes fall within the range of 10 to 40 nm, which was affected by the length and the bulkiness of POE segments.

A more interesting TEM examination is that a nanosized core-shell morphology was obtained when a TDI-POE urethane oligomer was employed as the seed for the polymerization of PPy. As far as the functionality of the synthesized nanoparticles is concerned, this study examined their intrinsic conductivity after separation from the dispersion medium and their effect on lithium ion conduction in an organic liquid medium. After separation, the particles existed as thin membranes that showed electrical conductivity of up to 10.3 Sm-1. When a very small portion of the nanoparticles (>0.1 wt%) was re-dispersed into a liquid electrolyte comprising a soluble lithium salt (LiX) and an acetonitrile solvent, e.g. DMSP, a limited change in the electrical conductivity was observed. However, the re-dispersion gave rise to a significant reduction in the electrical resistance at the electrode/electrolyte interface according to the gain-phase impedance measurement. By taking into account this effect, the influences arising from ILB (hydrophilic/hydrophobic balance) values of the brush chains, different types of the polyelectrolyte anions of LiX, variation of the acetonitrile solvents, and the different identity of the conducting polymers were evaluated.

SESSION C7: SEMICONDUCTOR NANOPARTICLES
Chair: L. Andrew Lyon
Wednesday Morning, November 29, 2000
Liberty (Sheraton)

9:00 AM C7.1
NANOCRYSTAL QUANTUM DOTS: RECENT PROGRESS IN SYNTHESIS AND SPECTROSCOPY
Munugi G. Bendaoud, Dept of Chemistry, MIT, Cambridge, MA

Advances in the chemical preparation of nanocrystal dots that are of high crystal quality have spurred detailed studies of their electronic, magnetic and optical properties. This talk will focus on three topics. The first focus will be the review of recent results in the synthesis of inorganic core nanocrystals. The second focus will be the study of the fluorescence properties of single nanocrystal quantum dots. Peeling away at the underlying effects inherent to spectroscopic studies of ensembles of dot, single dot experiments have discovered an unexpectedly simple behavior, much of which remains to be fully explained on a fundamental level. The third topic addresses the question of the possibility of laser action in chemically prepared nanocrystal quantum dots. Although an initial motivation for many optical studies, until recently and despite numerous efforts, stimulated emission from highly quantum confined chemically prepared dots had not been forthcoming.

9:30 AM C7.2
ATOMIC SCALE DEFORMATION OF COLLOIDAL PARTICLES UNDER HIGH ENERGY HEAVY ION IRRADIATION
T. van Dijk1, A. van Blaaderen1,2, W. F. van der Goot,3 A. Polman1
1FMF-Institute AMOLF, Amsterdam, THE NETHERLANDS
2Delft Institute, Utrecht University, THE NETHERLANDS
3Research Center Rosendaal, Dresden, GERMANY

MeV heavy ion irradiation changes spherical colloidal silica particles into non-spherical oblates. This deformation is due to a contraction of the particle in the direction of the ion beam and a linear expansion perpendicular to the ion beam. We studied this microtropic deformation effect of spherical silica colloids of both 300 nm and 1 μm diameter as a function of ion energy, fluence and flux, using Xe, Au and Cs ions. We used ion induced changes in the particle shape and fluences varying between 0.3 and 11x1015 ions/cm². Size aspect ratios as high as 5 are achieved. A linear increase of the transverse diameter is observed with increasing ion fluence. For a fixed fluence the deformation increases with ion energy and is linear with the average electronic stopping power. No volume change is observed after irradiation. The deformation effect decreases with increasing temperature. When the ion range is chosen less than the colloidal diameter, non-spherical shapes can be formed as well. Prolate particles can be obtained by subsequent irradiations under orthogonal angles. The deformation of TiO2, ZnS and ZnSiO3 core-shell particles will also be shown. Quite interestingly, no deformation is observed for crystalline Al2O3 and Ag colloids, as will be discussed. Finally, we will show several applications of these ion irradiation deformed particles. First, we find indication for nemtic liquid crystalline ordering of oblate particles in solution. Second, we observe large changes in the optical transmission spectra of a three-dimensional colloidal photonic crystal upon deformation.

9:45 AM C7.3
PREPARATION AND APPLICATIONS OF MULTI-SHELLED POLYMER BEADS

Functionalized polymer beads are important media for resin-bound synthesis, colloid chemistry, photonic bandgap, and materials science applications. Other applications in chemistry, physics, biology and medicine. A microdroplet fluorescence microscope makes it possible to study the spatially-dependent properties of the interior of such beads with high, three dimensional resolution. We have taken advantage of this ability to observe the interior of these beads to develop chemical techniques for seeds that are initially spatially homogeneous and patterned with large, chemically-distinct shells of controllable thickness. Dependent on the diameter of the beads, it is possible to make ten or more shells. We will discuss the techniques for the preparation of such layered beads and their application in combinatorial chemistry and materials science.

10:30 AM C7.4
COLLOIDAL QUANTUM RODS: Paul Allivier, Univ of California, Dept of Chemistry, Berkeley, CA

In recent years there have been significant advances in the preparation of semiconductor quantum dots by colloidal chemistry routes. CdSe and InAs are examples of materials which can be made in nearly spherical nanocrystals of high quality. We have recently learned how to control the shapes of these particles, to yield quantum rods. This provides a new opportunity to examine the influence of shape on optical, electrical, and structural properties. Colloidal quantum dots and rods may also find some practical applications, as biological fluorescent labels, or as the active elements in photocathodes.

11:00 AM C7.5
PREPARATION AND CHARACTERIZATION OF ONE-DIMENSIONAL CdS, CdSe AND GaN NANOPARTICLES

One-dimensional nanoparticles of CdS, CdSe and GaN semiconductors with different morphologies including rod-like [nanorods], wire-like nanowires, and cube-like [nanocubes] have been prepared using several different techniques. Their structural, electronic, and optical properties were studied using scanning electron microscopy [SEM], transmission electron microscopy [TEM], X-ray powder diffraction (XRD), electron diffraction (ED), energy dispersive X-ray spectroscopy [EDX], absorption, photoluminescence and Raman spectroscopy. The nanorods of CdS and CdSe were synthesized via arrested
precipitation from their respective morganic ions in a micellar solution. The materials showed straight and rodlike shapes with a narrow distribution of aspect ratio, which were confirmed from a VLS growth of gallium and ammonia. The SEM images indicated that almost all the resulting materials exhibited wire-like structures with diameters in the range of 20 to 50 nm and lengths up to several micrometers. The monomers of the TEM were prepared through the crystal growth of single self-assembled monolayers. The TEM image showed that each individual nanoparticles dispersed well on the carbon substrate and exhibits regular cubic-like shape. Our synthetic methods have provided new routes for the synthesis of semiconductor nanoparticles with a specific morphology. Potential applications of the nanoparticles in field emitting devices and single-electron transistors will be discussed.

11:15 AM C7.6
SELF-ORGANIZING PbSe QUANTUM CUBE AND QUANTUM DOTT SUPERLATTICES: W. Geelhoed, University of Amsterdam (AMRI) and IBM T.J. Watson Research Center, Yorktown Heights, NY; C.B. Murray, IBM T.J. Watson Research Center, Yorktown Heights, NY.

We report a high temperature (130 to 200°C) solution phase synthesis of monodisperse lead chalcogenide (PbSe, PbTe) quantum dots and quantum cubes. Organically passivated quantum dots with sizes tunable from 3 to 8 nm and quantum cubes with sizes tunable from 7 to 12 nm are isolated with ≤ 5% standard deviation. These dots and cubes show effects of quantum confinement with strong size-dependent absorption in the near IR. The dots and cubes each self-organize forming two and three dimensional superlattices (collodial crystals, opals). The symmetry of the superlattices is determined by the shape of the nanoscale building blocks. This provides opportunities to study the effects of shape on the electronic properties of quantum confined structures from "particles in a box" to "particles in a sphere."

11:30 AM C7.7
TEMPLATED FABRICATION OF HEXAGONAL ZnS SINGLE CRYSTAL NANOSHEETS A NEW MOLECULAR PRECURSOR FOR ZnS NANOPARTICLES BY A SOFT SOLUTION.

PROCESING ROUTE. Shia-Hong Yu, Jose Marich Calderon Moreno, Takashi Fujisawa, Takehiko Fujino, Ryo Teramishi, Misahiro Yoshimura Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Low-dimensional nanostructured semiconductors have been the focus of recent scientific research due to their important nonlinear optical properties, luminescent properties, and quantum size effects, which have a wide range of fundamental applications in nanodevices. Many attempts have been made to fabricate such low-dimensional nanostructure materials by use of a variety of nanofabrication techniques. Here, highly ordered lamellar ZnS single crystal nanosheets which we called "nanosheet," were fabricated for the first time by thermal decomposition of a new molecular precursor Zn(Sen), with a composition of Zn2Se4(NH2CH2CH2NH2) obtained via a soft solution processing route. The results of the decomposition were observable by a soft solution reaction of Zn2Se and thiourea or a similar reaction between Zn2 and S2- in ethylenediamine medium at 120-180°C. The powder X-ray diffraction and SEM images confirmed that this new molecular precursor displayed well-defined lamellar nanostructures. The thermal stability of this molecular precursor was determined by TGDTA analysis. After decomposed at 250°C the typical feature part, i.e., ethylenediamine molecule, pure hexagonal ZnS single crystals nanosheets with excellent lamellar nanostructure and highly (001) orientation were obtained. To our best knowledge, this is the first report about fabrication of unusual hexagonal ZnS single crystal nanosheets by a simple soft solution-processing route. In contrast, similar reactions in other solvents such as ethanol could only produce cubic ZnS nanoparticles. The optical properties of as-prepared cubic nanoparticles were investigated by monochromatic measurements. The results demonstrated that it is possible to fabricate low-dimensional anisotropic nanoparticles selectively by a soft solution-processing route, which may add another variable to tune the optical properties of semiconductor quantum dots.

This work has been supported by the Japan Society for Promotion of Science (JSPS) as part of the ‘Research for the Future Program’ No. RFTF01R00011.

11:45 AM C7.8
DESIGN AND MODELING OF PURPOSE-BUILT ANISOTROPIC METAL-OXIDE NANOMATERIALS. Lionel Vayssieres, Jinghan Guo, Joseph Nordgren, Uppsala University, Dept of Physics, Sweden.

A new concept has been developed in order to achieve a new generation of smart materials (i.e. purpose-built nanomaterials), modeled and designed to match the physical and structural requirements of its applications. This concept, well sustained by a thermodynamic model based on the monitoring of the nucleation, growth and ageing process through the control of the interfacial tension of the system allowing control the particle size and the surface morphology as well as to ability to thermodynamically stabilize metastable phases in solution. The outcome of such concept is of great interest both for fundamental and applied research purposes since the influence of parameters such as for instance, particle size, orientation and surface morphology, film texture and porosity on the electronic structure and/or catalytic activity of metal oxide materials may be probed and demonstrated. Moreover, designing well controlled materials to mimic the physical properties of existing devices as well as creating novel improved devices. This concept, well illustrated on the controlled growth of spinel iron oxide nanoparticles in aqueous solution, has been successfully applied to the development of novel well-designed anisotropic material such as large layers (several centimeter squares) of oriented (perpendicular and parallel) nanorods of iron(III) oxide (Hematite), zinc oxide microspheres and microtubes as well as at shrinkage ZnO materials deposited, without any templating method, onto various substrate, such as conducting glass, Si wafers or sapphire for photovoltaic and photocatalytic devices. New directions and applications such as, for instance, energy-related capacitors, electrochromic devices and nanostructured chemical and gas sensors are currently under investigation.

SESSION C8: DIELECTRIC NANO PARTICLES
Chair: Christine D. Keating
Wednesday Afternoon, November 29, 2000

1:30 PM C8.1
MONODISPERSE OXIDE NANOPARTICLES WITH APPLICATIONS IN FERROELECTRICS. Stephen O’Brien, Louis Brus, Columbia University, New York, NY; Chris B. Murray, IBM Corp. T.J. Watson Research Center, Yorktown Heights, NY.

The synthesis and structural characterization of relatively monodisperse nanoparticles of barium titanate (BaTiO3) is presented. The nanoparticles exist as an organic ligand-stabilized suspension in organic solvents for purposes of processing. The electric properties of thin films of barium titanate nanoparticles have been investigated. These ferroelectric and dielectric properties of BaTiO3 nanoparticles, in the perovskite structure are highly dependent on particle shape and size, especially approaching the nanoscale region. The spontaneous and reversible electric dipole moment, characteristic of ferroelectric metal oxides in an applied electric field, originates from ion displacement in the crystal unit cell. The behavior of this dipole moment in the bulk material is a function of ferroelectric domain size and domain-domain interactions. An understanding of this phenomenon would be considerably enhanced by the ability to study the ferroelectric properties of a material progressing from nanoscale (a limited number of unit cells) to bulk. It is therefore of importance to develop a synthetic nanochemistry of oxide nanoparticles which would allow control of particle size and shape, and allow manipulation into thin films or devices using chemical techniques.

2:00 PM C8.2
RESONANT LIGHT SCATTERING PROPERTIES OF METAL NANO SHELLS. Steven J. Oldenburg, Sarah L. Westcott, Joseph B. Jackson, Sarbhi Lal, Robin N. Taylor, and Naomi J. Halas, Department of Electrical and Computer Engineering and the Rice Institute, Rice University, Houston, TX.

Metal nanoshells are nanoparticles consisting of a dielectric core of nominally 100 nm diameter surrounded by a nanoscale (16-20 nm), uniform metallic shell. The plasmon-derived electromagnetic resonances of metal nanoshells are controlled by the relative dimensions of their core radius and shell thickness, while absolute size of the total particle determines whether it functions as an absorber or scatterer on resonance. Fabrication of gold nanoshells is based on functionalization of silica nanoparticles prepared by the Stober method, followed by electroless plating of gold onto the nanoparticle surface. For silica-core gold-shell nanoshells prepared by this method, the spectral range of the optical resonance of the final nanostructure extend from nominally 550 nm in the visible to beyond 2 microns in the infrared. In addition, the core-shell geometry gives rise to spectrally distinct multipole resonances, each with unique and strongly angle-dependent scattering properties. These polarization and angular dependence of the light scattering from specifically designed dipole and quadrupole resonant nanoshells has been measured, and very good comparison with theory is obtained. Further modifications of the metal-dependent light scattering properties of gold nanoshells due to the presence of a conductive or dielectric layered substrate may also be discussed.
Additional degrees of freedom from the dimensional and compositional asymmetry in nanoscale amorphous particles inspire novel device concepts and allow exceptional flexibility in tailoring their properties for the development of commercially feasible devices. In this presentation, we report solid phase crystallization induced formation of planes of ordered Si nanocrystallites within Si/SiO<sub>2</sub> superlattices [Si<sub>n</sub>]. We show that under certain fabrication conditions, Si nanocrystals have identical sizes, brick-like shapes, and preferred [111] crystalline orientation along the SL axis as determined by transmission electron microscopy and polarized Raman spectroscopy. The aspect ratio of this nanocrystalline object can be easily varied by changing the density of nucleation sites in amorphous Si (a-Si) layers with a specific thermal budget of rapid thermal annealing. Crystallographic anisotropy is expected to strongly affect the vertical transport through nanocrystals due to a six-fold symmetry of electron energy dispersion in Si. Si nanocrystals are very well passivated by SiO<sub>2</sub> vertically as follows from the geometry of the structure. On the other hand, laterally or in the X-Y plane, these a-crystallized nanocrystals are separated from each other by grain boundaries of a-Si residue. Lateral passivation, or in other words cross-talk among charged nanocrystals can be modified by post-crystallization oxygen diffusion and oxidation. The combined effects of shape, orientation and passivation anisotropy in the ensemble of nearly identical Si nanocrystals lead to a narrower photoluminescence compared to the luminescence signal from isotropic, nearly spherical Si nanoparticles. Fabrication of anisotropic Si nanocrystallites by solid phase crystallization of a-Si/SiO<sub>2</sub> SLAs shows an abundance of unique properties and a great promise of their successful implementation in nanoelectronic devices.

2:30 P.M. **C8.4**

**LAYER-BY-LAYER ELECTROSTATIC SELF-ASSEMBLY OF LARGE DIAMETER MONODISPERSE SILICA NANOSPHERES WITH A POLYELECTROLYTE:** Thomas S. Pho-Bolin, Isabel Galeski, and Reto Papadimitrakopoulos, Department of Chemistry, Polymer Science Program, Nonmaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

Recent efforts have focused on 2D and 3D assemblies with the goal of creating highly ordered supramolecular structures. We presently report results from the layer by layer electrostatic assembly of monodisperse silica spheres with particle diameter (D) from 100 to 400 nm with polyelectrolyte (PEI). Our results indicate that both thickness and surface coverage are pH-dependent. The average film thickness, as determined by ellipsometry, is as high as two third of the particle diameter per layer of SiO<sub>2</sub>/PEI. The structure and mechanical properties of these organic/inorganic superlattices have been characterized by scanning electron microscopy and quartz crystal microbalance spectroscopy. Control of pH and substrate quality could yield in highly uniform layers consisting of a monolayer of silica spheres. Such assemblies exhibit Bragg diffraction in the visible range. Implementation of these assemblies for semipermeable membranes with optical response could open new dimension in the conformal growth of meso-sized composites on a variety of technologically important applications.

3:15 P.M. **C8.5**

**ELECTRIC FIELD ASSISTED ASSEMBLY OF METALLIC NANOWIRES FOR CHARACTERIZATION OF MOLECULAR ELECTRONIC DEVICES:** Thomas S. Meyer, Thomas N. Jackson, Department of Electrical Engineering, Penn State University, University Park, PA; Christine Koning, Thomas E. Mallouk, Department of Chemistry, Penn State University, University Park, PA.

Recent interest in molecular-scale electronics as a means to fabricate extremely dense logic and memory circuits has led to the development of molecular diodes, switches, and negative differential resistance devices. These devices have been fabricated by self-assembly of the constituent molecules onto micron-scale (1 - 10 μm) metal pads defined on a planar substrate or nanometer-scale (50 - 70 nm) metal pads defined on a suspended silicon nitride membrane. In this talk, we will describe our recent research activities related to synthesis and electric field assisted assembly of nanometer-scale (15 - 200 nm) metallic wires, which provide an approach for probing molecular junctions at a smaller scale. The high aspect ratio nanowires are made using replication techniques where single or multiple layers of metals such as Au, Pt, Ag, and Pd are deposited onto a porous membrane and released into a dielectric fluid for assembly. Because the nanowires are compatible with molecular self-assembly strategies, molecular junctions can be formed within the nanowire during synthesis or between two crossing wires at the time of assembly. Assembly of the nanowires is conducted by introducing a nonuniform alternating electric field between two metal electrodes defined on a SiO<sub>2</sub> substrate. The forces that induce alignment of the nanowires are a result of nanowire polarization in the applied electric field. Using this technique, we have successfully positioned individual and crossed nanowires between metal pads that are used for external probing. Experiments are currently underway to measure the transport properties of the metallic nanowires and molecular junctions created within nanowires and at the intersection of the crossed nanowires.