SYMPOSIUM CC

Photophysical Properties of Monolayers on Nanomaterials and Surfaces

November 28 - December 1, 2005

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* Invited paper

SESSION CC1: Metal Nanoparticles - Electronic Properties
Chair: Lucia Pasquato
Monday Morning, November 28, 2005
Room 300 (Hynes)

8:30 AM *CC1.1
Dithiocarbamates: a promising metal binding group for molecular electronic devices. Jurina Wessels[1], Florian von Wrochem[1], Peter Morf[2], Heinz-Georg Nothofer[1], Frank Scholz[1], Williem Ford[1], Thomas Jung[2] and Akio Yasuda[1]; [1]Sony Deutschland GmbH, Stuttgart, Germany; [2]Paul Scherrer Institute, Villigen, Switzerland.

Substantial research work currently investigates nanoscale electronic devices based on organic molecules. However, one of the major tasks in molecular electronics is to understand how the coupling of the molecules to the metal contacts and the molecular structure influence the current-voltage response of molecules within a contacting gap. Due to the nature of metals and molecules, the metal-molecule interface generally resembles an intrinsic barrier for charge transport and leads to a large potential drop across the interfaces. In this presentation, we introduce dithiocarbamates as metal binding groups, which provide an excellent electrical contact to gold electrodes, and present conclusive experimental and theoretical evidence for well-defined self-assembled monolayer formation and the electronic behaviour of dithiocarbamate groups. The experimental results will be supported by combined ab-initio calculations performed at the DFT level. The influence of the molecular structure and the importance of the metal-molecule interface on the conductivity of molecule-cluster systems will be discussed in light of the resulting electronic structure.

9:00 AM *CC1.2
Electric Properties of Organized Gold Nanoparticles.
Guenter Schmid, Inorganic Chemistry, University of Duisburg-Essen, Essen, Germany.

The organization of ligand protected gold nanoparticles in two dimensions (2D) can be performed either by self-assembly or by spincoating techniques. Multilayer systems, build up of Au55 double- and monolayers with various ligand shells and SiO2 barrier films of varying thickness, have been generated and investigated. Especially the electric characteristics have been studied in detail. Monolayers and double layers systems behave very different with respect to their inter-layer behaviour: whereas double layers interact by dipolar forces, the cluster monolayers communicate with each other by electronic tunnelling processes through the SiO2 barriers. Tunnelling distances of up to 5.7 nm could be registered. Charge transport mechanisms between Au55 clusters have also been studied using organic ligand molecules of different lengths as distance holders. There is a significant difference between mechanically and ionically separated clusters and those that are covalently linked. The activation energies for electron transitions in covalently linked cluster assemblies are considerably lower than those in non-covalently organized systems. Here, the cluster-cluster distances clearly dominate the activation energies. These observations can be compared with H. Taube's famous inner and outer sphere mechanisms in redox processes of transition metal complexes.

9:30 AM CC1.3
Dendronized Conjugated Ligands and Hybrid Nanoparticles: Distance and Generation Dependent Energy Transfer and Electron Transport Properties. Rigoberto Advincula and Suxiang Deng; Department of Chemistry, University of Houston, Houston, Texas.

We describe the synthesis and characterization of hybrid organic polymers-nanoparticle materials with interesting energy transfer and electron transport properties. The goal is to combine the properties and processability of these materials for electro-optical device and sensor applications. By tuning the band-gap and the conjugation lengths of the organic component, various resonances and energy transfer mechanisms can be observed between semiconductor and or metal nanoparticles. We have investigated the tethering of polythiophene dendrons directly to semiconductor nanoparticles which resulted in improved processability as well as interesting electro-optical effects. The polythiophene dendrons were synthesized via a series of coupling reactions in a convergent approach. Various spacers and ligands (thiol and phosphonate) were utilized for binding. The distance and generation of dendron to the metal and semiconductor nanoparticle surfaces are critical for device functionality. Various surface sensitive analytical techniques have been utilized to analyzed film formation and deposition including combined surface plasmon spectroscopy and fluorescence measurements.

9:45 AM CC1.4
Directed Assembly of Ligand-Coated Nanoparticles into Linear Chains of Controllable Composition.
Gretchen A. DeVries, Brenda Long, Isabella R. Franchini and Francesco Stellacci; DMSE, MIT, Cambridge, Massachusetts.

The optical and electronic behavior of a nanomaterial depends not only on the dimensions of the material but also on its orientation and its interactions with other nanomaterials. For instance, it is well known that the surface plasmon absorption of a closely spaced pair of metal nanoparticles occurs at lower energy than that of isolated nanoparticles due to interparticle coupling. In order to observe and manipulate such interparticle interactions, it is necessary to develop a method to control the placement of nanoparticles relative to each other. Ligand-coated metal nanoparticles are particularly interesting, both because the ligands affect the physical properties of the nanoparticles and because the ligands can be used as handles for self-assembly of the particles. In this work, we demonstrate directed assembly of mixed-ligand nanoparticles by taking advantage of ordered domains that spontaneously form in the ligand shell. As a result of this molecular-level ordering, we are able to functionalize these nanoparticles in specific locations with a third type of molecule, enabling the assembly of the particles into larger structures. For example, by placing two carboxylic acid terminated ligands in diametrically opposed positions on the nanoparticles and reacting them with diamine-terminated molecules, linear chains of nanoparticles joined by peptide bonds are generated. Appropriate choices for the functionalization chemistry allow us to control the precise composition of the chains; for example, we can synthesize chains that consist of alternating gold and silver nanoparticles, or of nanoparticles of different sizes. Analysis of the optical response of these nanoparticle chains demonstrate plasmonic coupling among the particles in the chain that is dependent on the composition of the chain.

SESSION CC2: Ligands and Nanoparticles
Chair: Molly Stevens
Monday Morning, November 28, 2005
Room 300 (Hynes)

10:30 AM *CC2.1
Self-Assembled Monolayers on Metal Nanoparticles: The Effect of Core Size. Lucia Pasquato, [1]Dep. of Chemical Sciences, University of Trieste, Trieste, Italy; [2]Trieste Section, INSTM, Trieste, Italy.

Since more than ten years1 the passivation of gold nanoparticles by an organic monolayer opened a new era in the study of these nano-materials and in developing new applications. A great deal of novelties derived from the possibility to exploit the intrinsic chemical, electronic and optical properties of the nano-sized metallic core. On the other hand, the presence of a self-assembled monolayer has developed fascinating complex and functional molecular assemblies to generate novel devices and materials, potentially useful for sensing, catalysis, transport, and other applications in medicinal or engineering science. However, many aspects and properties of the monolayer are still unknown or not fully understood. Monolayer protected nanoparticles constitute one further example of membrane mimetic systems. They present the peculiarity of an extremely slow exchange of the monomers and of a limited mobility in the monolayer, thus allowing to define precisely radial subregions of different polarity. This limited mobility is at the basis of their behavior as multivalent systems showing cooperativity in the recognition of substrates or in performing catalytic processes.2 The recent accessibility of water soluble systems has expanded their field of application also to this solvent where hydrophobic interactions become dominant. We will show that EPR spectroscopy may be utilized to obtain useful information on the specific question of the interaction of an hydrophobic probe with the monolayer of water soluble Au-MPC. For example we have determined the partition isotherms and exchange rates of a radical probe between an aqueous solution and the monolayer of water soluble Au-MPC and, more we could quantified the effect of core size on the partition of organic solutes in the monolayer of water soluble nanoparticles. 1. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. Chem. Soc., Chem. Commun. 1994, 801-802. 2. Pasquato. L.; Pengo, P.; Scrimin, P. J. Mater. Chem. 2004, 14, 3481-3487.

11:00 AM CC2.2
Phase Separation on Mixed Monolayer Protected Metal Nanoparticles: a study by Infrared Spectroscopy.
Andrea Centrone[1,2] and Francesco Stellacci[2]; [1]Chimica, Materiali ed Ingegneria Chimica "G. Natta", Politecnico di Milano, Milano, Italy; [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Monolayer protected metal nanoparticles (MPMNs) are composed of a metallic core coated by a self-assembled monolayer (SAM) of thiolated molecules (ligands). On flat surfaces, SAMs composed of mixture of ligands phase separate into randomly ordered domains. Scanning tunneling microscopy studies have shown that similar mixed SAMs when assembled on MPMNs phase separate into ordered ring shaped domains [1] that can be just one- or two-molecules wide. Here we present a series of infrared spectroscopy studies aimed at the characterization of the molecules present in the ligand shell of these mixed ligands MPMNs. IR spectroscopy probes molecular vibrations in localized and in extended molecular domains. Being sensitive to intra and intermolecular interactions, it is commonly used to probe molecule conformations and environments. Gold nanoparticles, coated with various mixtures of 1-octanethiol (CH3-(CH2)7-SH) and mercaptopropionic acid (HOOC-(CH2)2-SH) have been studied. Evidences of phase-separation on the ligand shell have been found mainly analyzing the C-H stretching vibrational modes. A complete analysis of the conformation of the molecular ligands as a function of composition will be presented. [1] A. M. Jackson, J. W. Myerson and F. Stellacci, Nature Materials, 3 (2004) 330-336

11:15 AM CC2.3

Self-Assembled Monolayers Revisited: How the topology of a nanoparticle can change "almost" everything.

Alicia Marie Jackson and Francesco Stellacci; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Monolayer protected metal nanoparticles (MPMNs) are composed of a metallic core (typically a single crystal) coated by a self-assembled monolayer (SAM) of thiolated molecules. The organic coating plays a key role in determining most of the particles' properties such as solubility, assembly and sensing. To date, little has been experimentally observed on the true conformation of the molecules that compose the ligand shell. In this talk we will show scanning tunnelling microscopy evidences that SAMs on nanoparticles differ significantly from equivalent SAMs on flat surfaces, both in the cases of one and two-component monolayers. The experimentally observed ligand head-group spacing has been used to determine the spacing of the sulfur atoms at the gold nanocrystal surface. For homoligand particles, we find that, as predicted by theoretical models, this spacing is significantly smaller than the one observed for SAMs on flat surfaces and varies with particle size. Specifically, we have found that octanethiol coated gold particles show an average sulfur-sulfur spacing of ~ 4 $\AA$, significantly less than the 5 $\AA$ spacing on flat Au(111) surfaces. This indicates a high packing density at the base of the molecules, whose consequences on SAM stability and place-exchange reactions will be discussed. In the case of mixed-ligand nanoparticles, SAMs that phase-separate into random domains on flat surfaces, assemble into regular and ordered domains on the surfaces of the particle driven by the high curvature of the core [1]. In the case of a binary mixture on nanoparticles, a few molecules wide ring-shaped domains of alternating composition form. Here we present new findings that show the dependence of the domain width on the nanoparticle core size. The presence of these molecular scale domains has significant consequences on the particle properties, such as solubility and resistance to protein nonspecific adsorption. Additionally, for both homoligand and mixed-ligand nanoparticles, we observe a discrete change in sulfur-sulfur spacing at a critical nanoparticle diameter. Our results are in good agreement with both spectroscopic data and theoretical models, and indicate the importance of the particles' radius of curvature in determining the structure of the surrounding SAM. [1] A. M. Jackson, J. W. Myerson, F. Stellacci, Nature Materials 3 (5): 330-336 MAY 2004.

11:30 AM *CC2.4

Functionalized Nanoparticles and Nanoparticle Arrays: Tuning Properties through Ligand Exchange.

James E. Hutchison, Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon.

Many of the properties of metal nanoparticles and their arrays depend upon the ligand shells that surround the metal core. In addition to providing stabilization and solubility, these organic monolayers provide added functionality, serve as an interface to macroscopic structures and provide an interface between nanoparticles in an array. The nature of the interface between nanoparticles and other structures is important in harnessing the interesting electronic and optical properties of nanoparticle materials. In this presentation several approaches to producing 1-, 2-, and 3-D nanoparticle assemblies on surfaces or in solution will be described. Gold nanoparticles (having core diameters of 0.8, 1.5 or 10 nm) produced by convenient chemical syntheses are functionalized through ligand exchange reactions that permit the introduction of a wide range of surface functional groups around the periphery of the nanoparticles. These functional groups are used to direct assembly of linear arrays and 2-D films of nanoparticles on solid substrates. In solution, well-defined aggregates of the nanoparticles are prepared by selective cross-linking of the exterior functional groups. In each case, the electronic and optical properties of the assemblies are being investigated to determine the influence of the ligand shell, nanoparticle core structure and the internanoparticle interactions on these properties.

SESSION CC3: Nanoparticles I
Chair: Francesco Stellacci
Monday Afternoon, November 28, 2005
Room 300 (Hynes)

1:30 PM *CC3.1

Colloidal Nanocrystal Heterostructures with Complex Shape.

Paul Alivisatos, Lawrence Berkeley National Laboratory, Berkeley, California.

This talk will present recent work on the preparation of colloidal semiconductor nanocrystals with complex shapes. Using organic surfactants, it is possible to modulate the growth rate of different facets of a nanocrystal to produce rods, disks, and branched structures, such as tetrapods. It is also possible to grow new materials on the different facets that are presented, to create heterostructures. Recent studies of growth on the ends versus the sides of rods and tetrapods will be presented.

2:00 PM CC3.2

Optical Effects in Chromophore Functionalized Metal Nanoparticles.

Prashant V. Kamat[1,2,3] and K. George Thomas[1]; [1]Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana; [2]Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, Indiana; [3]Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana.

Nanocluster-molecular assemblies provide innovative strategies for designing next generation nanodevices. Of particular interest are photoresponsive organic-inorganic hybrids which when assembled as two- or three- dimensional architectures provide novel materials with tailored optical and photochemical properties [1-2]. Photoinduced electron transfer between gold nanoparticles and the chromophores has been investigated by femtosecond transient absorption spectroscopy as well as photoelectrochemical measurements. The electron transfer between the excited chromophore and the gold nanoparticle can be modulated by controlling externally applied potential. As the metal particles are charged, a decrease in the rate of electron transfer is seen. The influence of charging effect on the excited state behavior of chromophores on metal nanoparticles will be presented. Taking advantage of the charging properties of gold nanoparticles, a third generation photoelectrochemical cell based on visible absorbing dyes (porphyrin, chlorophyll a) and gold nanoparticles has been constructed. Superior performance of this cell compared to that without the gold confirmed the beneficial role that metal nanoparticles play in accepting and shuttling the photogenerated electrons from excited chromophore to the collecting electrode. Use of metal nanoparticles in improving the photoinduced charge separation efficiency of donor-acceptor type light harvesting assembly will also be discussed. References 1. Thomas, K. G.; Kamat, P. V., Chromophore Functionalized Gold Nanoparticles. Acc. Chem. Res., 2003, 36, 888. 2. Barazzouk, S., Kamat, P. V. & Hotchandani, S. Photoinduced Electron Transfer between Chlorophyll a and Gold Nanoparticles. J. Phys. Chem. B 109, 716-723 (2005).

2:15 PM CC3.3

The Effect of Titania Particle Morphology on Dye Adsorption for Photovoltaic Applications.

Judith D. Sorge and Dunbar P. Birnie; Ceramics and Materials Engineering, Rutgers University, Piscataway, New Jersey.

This research centers around comparing the chemical and physical properties of dye attachment to different morphologies of titania particles. Titania is used as an electrode in dye sensitized solar cells, and determining the method of dye attachment and whether there are preferential areas of dye bonding should prove useful for increasing the efficiency of cells in the long term. Spherical titania particles are formed by sol-gel methods, and various processes are used to either change the aspect ratio of the spherical particles or produce different shaped particles originally. These methods include oriented attachment, self assembly and chemical transformation. Dye particles for solar cells involve a ruthenium complex, so these same dyes are used to determine the bonding and attachment. It has been shown that the efficiency of the solar cells increases with surface area due simply to a larger amount of electrons being excited in the dye, but studying the dye bonding should allow the opportunity to understand if this efficiency can be increased through the chemistry of the cell as well. The adsorption of dye molecules is studied by two methods, a crystallographic comparison and by determining the relative efficiency of a solar cell. The crystallography of the various titania particles is determined by TEM, and then dye is adsorbed on a titania single crystal with the same orientation to determine dye bonding properties. Characterization is done by absorption spectra and the relative changes in the spectra will confirm if there is preferential bonding in certain crystallographic directions. Then the relative efficiencies of dye sensitized solar cells can be measured to determine the effect of morphology on the device performance due to changes in conductivity and dye adsorption.

SESSION CC4: Chromophores and Nanoparticles

Chair: Thomas K. George
Monday Afternoon, November 28, 2005
Room 300 (Hynes)

3:30 PM *CC4.1

Cornell Dots: Bright and Stable Fluorescent Silica Core-Shell Nanoparticles. Ulrich Wiesner, Materials Science & Engineering, Cornell University, Ithaca, New York.

Fluorescent nanoparticles offer enormous scientific and technological promise as labels and photon sources for a range of biotechnological and information-technology applications such as biological imaging, sensor technology, microarrays, optical computing, and display technology. Many applications require size-controlled, monodisperse, bright nanoparticles that can be specifically conjugated to biological macromolecules or arranged and positioned in higher-order structures and devices. As an alternative to single molecule fluorophores and quantum dots, silica-based particles derived through the Stoeber process hold particular promise since they are water soluble, the silica chemistry is well established, simple and extremely versatile, and silica is compatible with semiconductor processing. Here we report on a program at Cornell to develop a novel class of multifunctional silica-based fluorescent core-shell nanoparticles, referred to as Cornell- (or C-) dots, using a synthesis based on the Stoeber method that can easily be scaled up to produce large quantities. The proposed program identifies ways in which the intrinsic properties of the new Cornell-dots can be engineered and tailored starting from a molecular-level understanding of the photo-physical effects. Such properties include, for example, the emission and absorption spectrum, the radiative rate, and the nonlinear optical response. While substantial progress has been made with the best known example of this photonic engineering, semiconductor-based quantum dots, their application suffers from various limitations due to uncontrolled surface states and surface chemistry and to their toxicity. The flexibility in fine-tuning dye and dye-matrix chemistries as well as particle architecture and surface chemistries has the potential to overcome these disadvantages and to open the door to innovative particles and assemblies whose optical properties can be controlled in ways not possible with previously studied particle systems. Reference: H. Ow, D. R. Larson, M. Srivastava, B. A. Baird, W. W. Webb, U. Wiesner, Bright and Stable Core-Shell Fluorescent Silica Nanoparticles, Nanoletters 5 (2005), 113-117.

4:00 PM *CC4.2

Organic Chromophore/Metal Nanoparticle Composite Systems: Optical Properties. Joseph W. Perry, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Coupling of organic chromophores to metal nanoparticles can lead to dramatic plasmonic enhancement of two-photon absorption and fluorescence. We report on metal nanoparticles of various morphologies coated with chromophoric ligands and their two-photon properties. For chromphores bound to silver nanoparticle-based fractal clusters, five orders-of-magnitude enhancement is observed in the two-photon cross section under plasmonic enhancement conditions. Chromophoric molecules can be self-assembled in large numbers ($\sim$2,500) onto individual silver nanoparticles to provide ultrabright fluorescent nanobeacons, even under non-resonant conditions with the particle plasmon. These particles have been tailored for solubility in a variety of solvents, including water, and can be functionalized with bioactive groups for specific labeling applications. We have also developed metal nanoparticle based composites for two-photon 3D lithography. These composites have enabled the direct two-photon writing of metallic micro- and nano-structures that may be useful for a variety of applications.

4:30 PM *CC4.3

Fluorophore Covered Gold Nanoparticles. Luca Prodi, Francesco Zerbetto, Marco Montalti, Nelsi Zaccheroni and Gionata Battistini; Dipartimento di Chimica "G. Ciamician", University of Bologna, Bologna, Italy.

Gold colloids showed their versatility since their stabilization by surface modification was achieved by Brust and coworkers. [1] Passivation with thiols, in fact, allowed to bind almost any kind of molecule to the metal clusters and to exploit the unusual optical and electronic properties of gold colloid in the design of new nanostructured materials. [2] In this context particular interest was devoted to the understanding of the interaction between gold clusters and the appended units. We dedicated particular attention to the study of the organization of pyrene containing thiols and amines on the surface of the gold colloids. [3,4] Thanks to the influence on the luminescence properties of the pyrene-nanoparticle and pyrene-pyrene interactions it was possible to gain important pieces of information about the structure of the stabilizing monolayer and on the efficiencies of the photophysical processes occurring in the derivatized nanoparticle. Moreover, by controlling the surface density of the fluorophore and the length of the alkyl backbones., we were able to modulate the overall fluorescence properties of the system. We also investigated gold clusters derivatized with a terpyridil unit. In this case we observe a great stabilization of the nanoparticles upon zinc complexation; also in this case photoluminescence was able to provide useful information on each step of surface modification . [1] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Commun. (1994), 801 [2] K.G. Thomas, P. Kamat, Acc.Chem.Res. 36 (2003), 888. [3] M. Montalti, L. Prodi, N. Zaccheroni, R. Baxter, G. Teobaldi, Langmuir, 19, (2003), 5172. [4] M. Montalti, L. Prodi, N. Zaccheroni, G. Battistini, Langmuir, 20, (2004) 7884.

SESSION CC5: Ligands and Nanoparticles' Shape

Chair: Xiaogang Liu
Tuesday Morning, November 29, 2005
Room 300 (Hynes)

8:00 AM *CC5.1

Coherent Lattice Oscillations in Gold Prismatic Monolayer Nanocrystal Arrays Made by the Nanosphere Lithographic Technique. Wenyu Huang, Wei Qian and Mostafa A. El-Sayed; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

Using the Van Duyne technique of nanosphere lithography, monolayer arrays of prismatic gold nanocrystals of different sizes are prepared. Using femtosecond transient bleach spectroscopy, the intensity of the bleach resulting from the coherent excitation of the electronic surface plasmon absorption is monitored at different times and at different wavelengths. The relaxation of the coherent electronic excitation results in coherent lattice vibration of the symmetric breathing modes of the prismatic nanocrystals whose frequency is determined from the observed periodic change in the bleach intensity at a certain wavelength. The dependence of the oscillation frequency on size is determined. From the dependence of the amplitude and phase of the periodic change of the bleach intensity on the monitoring wavelength, the change in the nanoparticle size during the vibration is estimated. The photothermal behavior of these prisms is determined from the SEM study of the laser power dependence.

8:30 AM *CC5.2

The Roles of Capping Agents in Shape-Controlled Synthesis of Metal Nanostructures. Younan Xia, Chemistry, University of Washington, Seattle, Washington.

This talk will discuss the roles played by various capping agents in the shape-controlled synthesis of metal nanostructures. I will focus on the silver system, although the conclusions might be extendible to other noble metals. In general, a capping agent might have the following funtions: 1)stabilization of a colloidal suspension; 2)alteration of the growth rates of various facets of a particle via selectively adsorption; 3)promotion of oxidative etching through coupling with oxyegn in air; and 4)accelaration or retardation of the reduction of metal ions via coordination. All these factors play important roles in generating metal nanostructures with well-controlled sizes, shapes, and crystallinity. I will focus on the fundamental mechanisms, as well as potential extensions.

9:00 AM *CC5.3

The Effect of Surfactant-Mediated Restructuring on the Magnetic and Optical Behavior of Nanoparticles. Jess Patrick Wilcoxon[1], Billie Abrams[1] and Eugene Venturini[2]; [1]Advanced Materials Sciences, Sandia National Laboratories, Albuquerque, New Mexico; [2]Nanostructure and Semiconductor Physics, Sandia National Laboratories, Albuquerque, New Mexico.

Nanoparticles synthesized in solution are invariably stabilized using organic surfactants which bind to cluster surface sites and prevent cluster aggregation. The binding of the surfactant to the metal atoms at the cluster surface weakens the bonds to the other atoms, making the surface atoms particularly mobile. So, in solution, diffusion, cluster collisions, and exchange of surface atoms bound to ligands can be facile. This can alter the cluster size distribution, and optical and magnetic properties with sample age.[1,2] We report investigations of cluster/surfactant binding using size-exclusion chromatography, (SEC), to separate clusters by size, and chemical affinity chromatography, (CAC), to investigate the effect of ligand binding to the cluster surface. Studies of the effect of surfactant binding using CAC on the optical and magnetic behavior are described for noble metal clusters, (Au, Ag, Cu and binary alloys), and base metal clusters, (Co, Fe, Ni and alloys), respectively. Some surfactants like alkyl thiols and amines are observed to etch the cluster surface and dramatically alter the size distribution as measured by SEC, often narrowing it with time. We find that the strength of the surfactant-metal binding determines whether etching occurs. [1] J.P. Wilcoxon, P. Provencio, J. Phys. Chem. B 107, 12949-12957, (2003). [2] J.P. Wilcoxon, E.L. Venturini, and P.P. Provencio, Phys Rev B, 69, 172402, (2004). Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

9:30 AM *CC5.4

Wet Chemical Functionalization of Metal Nanorods. Catherine J. Murphy, Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina.

Gold and silver nanorods and nanowires of controllable aspect ratio have been prepared by a surfactant-directeed method in water, in air. The cationic surfactant head group and tail length both contribute to the final morphology of the metal nanoparticle. The surfactant makes bilayers on the sides of the rods, and further functionalization with thiols can occur at the ends of the nanorods and link nanorods end to end. The cationic surfactant bilayers can also be wrapped up with polymers in a layer-by-layer electrostatic approach. In the absence of surfactant, silica coatings of controllable thickness can be made around the nanorods and nanowires.

SESSION CC6: Nanoparticles II
Chair: Prashant Kamat
Tuesday Morning, November 29, 2005
Room 300 (Hynes)

10:30 AM *CC6.1

Thermal and Photophysical Properties of Functionalized Nanoparticles and Nanoparticle Assemblies. Paul V Braun, Zhenbin Ge, Robert G. Shimmin and David G. Cahill; Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

We have performed a number of studies on the effect of organic ligands on the thermal and photophysical properties of nanoparticles and nanoparticle assemblies. Thermal transport in aqueous and non-aqueous suspensions of functionalized Au and AuPd nanoparticles is investigated by time-resolved measurements of optical absorption. The thermal properties of the ligand shell are found to be a strong function of both the solvent and monolayer. The thermal coupling between the AuPd nanoparticles and water is strong regardless of the self-assembled stabilizing group, while the thermal coupling in non-aqueous and mixed solvent systems can be considerably lower. Model systems consisting of self-assembled monolayers on planar substrates are also being investigated. The photophysical properties of more complex nanoparticle structures formed through directed assembly will also be discussed. These include Ge nanoparticles assembled within colloidal crystals, hydrophilic and hydrophobic Au nanoparticles assembled within liquid crystals, and charged Au nanoparticles assembled using protein templates.

11:00 AM CC6.2

Surface Chemical Modifications of Silicon and Germanium Nanowires. Song Jin and Pinray Huang; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

One-dimensional nanostructures such as semiconductor nanowires (NWs) are being intensively studied for both the fundamental and technological interests. Despite the nearly exponential growth of nanowire research, molecular surface chemistry of semiconductor NWs has not been systematically investigated. Yet surface is of extreme importance to the physical properties and device performances of semiconductor NWs. We investigate how molecular surface modifications of silicon and germanium nanowires impact their physical properties. Silicon (germanium) nanowire surfaces are modified using hydrosilylation (hydrogermalytion) reactions with a monolayer of organic molecules via Si-C (Ge-C) bonds and conveniently probed using highly sensitive nanodevices such as nanowire field-effect transistors. We expect the passivation of NW surfaces to drastically improve electrical characteristics, such as improved mobilities and reduction of hysteresis, since elimination of defective Si/SiOx interface and dangling bonds reduces surface scattering and trap states. Ultimately, we hope to fine-tune NW physical properties systematically by engineering surface functional groups.

11:15 AM CC6.3

Connecting Optical Performance to the Molecular Structure of Nanoparticle-Films. Jeffy Jimenez, Kevin Young, Alessandro Anzalone and Norma Arcelia Alcantar; Chemical Engineering Department, University of South Florida, Tampa, Florida.

Nanomaterials and nanotechnology have been widely investigated because of their potential applications as LCD screens, semiconductors, and chemical catalysts, among others. The special photoluminescence of these materials is based upon their ability to absorb and emit light energy in a certain range of the visible spectrum. The interest of this research is focused on the study and characterization of cadmium selenide (CdSe) nanoparticle-thin films, looking at their optical behavior when exposed to different normal pressures and shearing conditions. This property is enhanced when the nanoparticles are perfectly distributed in a thin film. These films are assembled with a Langmuir-Blodgett trough, allowing the deposition of a thin layer atop various substrates. Several techniques have been used to characterize such films. For instance, atomic force microscopy (AFM) is utilized to characterize the surface topography. The surface forces apparatus (SFA) is used to determine the effects of shearing velocity and normal pressure on the light absorption and photoluminescence intensity of such films. The results from the SFA also show that the tribological properties (i.e., lubrication, wear and friction) of CdSe films highly depend on their surface densities. The results of this project establish a safe range of accepted stress within which the luminescent properties of the CdSe particles are not aversely affected.

11:30 AM *CC6.4

The Role of the Surface and Surface Ligands in the Doping of Semiconductor Nanocrystals. Lijun Zu[1], David J. Norris[1], Steven C. Erwin[2], Michael I. Haftel[2], Thomas A. Kennedy[2] and Alexander L. Efros[2]; [1]Dept. of Chemical Engineering & Materials Science, Univ. of Minnesota, Minneapolis, Minnesota; [2]Naval Research Laboratory, Washington, District of Columbia.

This talk will address the intentional incorporation of impurities (or dopants) into semiconductor nanocrystals. While a variety of doped nanocrystals have been synthesized, no detailed understanding exists about how this process works or how it can be controlled. Moreover, it is not clear why it is possible to introduce impurities into some semiconductor nanocrystals but not into others. These difficulties have hindered the development of a whole class of new materials, including n- and p-type nanocrystals. Here we present a new model based upon kinetics that addresses the doping problem. In particular, we use Mn-doped II-VI semiconductor nanocrystals as a model system to show that: (i) the binding of the impurity to the nanocrystal surface plays a key role in the doping process and (ii) the surfactants in the growth solution can inhibit doping by competitively binding with the impurity. After verifying the central principles of this model, we then use its predictions to incorporate Mn into previously undopable CdSe nanocrystals. Thus, this model should provide guidance for obtaining a variety of doped semiconductor nanocrystals.

SESSION CC7: Nanoparticles' Coatings
Chair: Paul Braun
Tuesday Afternoon, November 29, 2005
Room 300 (Hynes)

1:30 PM *CC7.1

Spontaneous Assembly of Plasmon Waveguide Nanostructures from Block Copolymer Surfactants and Nanoparticles. Youngjong Kang, Chao Zuo and T. Andrew Taton; Chemistry, University of Minnesota, Minneapolis, Minnesota.

Assembly of nanoparticles into higher ordered structures can lead to distinct, collective physical properties which are not exhibited by single or randomly arranged nanoparticles. For example, the unique scattering behavior of one-dimensional chains of regularly spaced, metal nanoparticles allows them to serve as effective conduits of visible light, even though they are ten times narrower than visible wavelengths. We report a solution-phase approach to generating nanoparticle plasmon waveguides by (1) encapsulating single nanoparticles within spherical, block-copolymer micelles, and then (2) triggering a sphere-to-wormlike micelle transition that causes the encapsulated particles to be arranged in regular chains. Because the precursor spherical micellar shells are crosslinked, the morphological transition of these micelles into cylindrical shapes is frustrated. As a result, the particles are still surrounded fully by polymer, and the interparticle distance is determined by the initial thickness of the shell. We have demonstrated that this method can be used to grow nanoparticle chains up to tens of microns in length, for various nanoparticle sizes and polymer shell thicknesses. We propose that this approach can be used to fabricate bulk quantities of plasmon waveguides for deposition or assembly in optoelectronic circuitry, where miniaturizing optical components is an important challenge.

2:00 PM CC7.2

Chelating Ligands for the Surface Functionalization of Colloidal Nanocrystals. Peter Reiss[1], Claudia Querner[1], Joel Bleuse[2] and Adam Pron[1]; [1]DRFMC/SPrAM, CEA Grenoble, Grenoble, France; [2]DRFMC/SP2M, CEA Grenoble, Grenoble, France.

A new family of ligands, namely alkyl or aryl derivatives of carbodithioic acids (R-C(S)SH), is proposed for the surface functionalization of colloidal nanocrystals. These ligands offer several advantages: 1) They are applicable to various types of nanocrystals containing "soft" metal atoms, including II-VI semiconductors and gold. 2) They quasi-quantitatively exchange initial surface ligands in very mild conditions as evidenced by NMR spectroscopy. 3) They considerably improve the resistance of nanocrystals against photo-oxidation because of their ability of strong chelate-type binding to surface metal atoms. This has been quantified by comparative spectroscopic studies on CdSe based core and core/shell systems carrying TOPO, thiol and carbodithioate ligands. The relatively simple synthesis of carbodithioate ligands via Grignard intermediates opens up new possibilities in nanocrystals' surface engineering through the design of bifunctional ligands. Such ligands contain a second functional group, separated from the anchoring dithioate function by an appropriate spacer. This group can be chosen, for example, to controllably tune the solubility of the nanocrystals in a desired solvent or as a specific site for the grafting of other molecules or macromolecules on the nanocrystal's surface. We illustrate the latter approach with the example of grafting electroactive oligoanilines or oligothiophenes on CdSe nanocrystals, discussing not only the synthetic pathway but also presenting spectroscopic and electrochemical properties of these new organic/inorganic hybrids.

2:15 PM CC7.3

Photoluminescence Enhancement of CdTe Nanocrystals through a Ligand Exchange Process. Takaaki Tsuruoka, Masanori Sugiyama, Kensuke Akamatsu and Hidemi Nawafune; Konan University, Kobe, Japan.

Ligand-protected semiconductor nanocrystals have received much attention over the past decade due to their size-dependent physical and chemical properties. The preparation of semiconductor nanocrstals with high QY is still real challenge in the applications to next generation optoelectronic devices. Further, the development of a method that allows effective surface modification of semiconductor nanocrystals with diverse surface functionalities would be extremely beneficial for the development of electrical and optical devices. In this study, we report on the preparation of alkanethiol monolayer-protected CdTe nanocrystals with high fluorescence QY achieved by surface modification though ligand exchange reaction. The CdTe nanocrystals were synthesized in octadecene and diluted by toluene, and then alkanethiol molecules were added into toluene containing CdTe nanocrystals. Significantly, during the mixture was stored in the dark for several hours, the fluorescence QY of CdTe nanocrystals was improved from 1 % up to 45 % without any change in PL peak wavelength (600 nm). The surface structures of protective molecules of the nanocrystals were characterized by FTIR spectroscopy, demonstrating that the initially bound tributhylphosphine were exchanged with alkanethiol molecules during the reaction. Thus the increase in QY may be attributed to compensation of the defect site of the nanocrystal surface by attachment of alkanethiol molecules. The purified CdTe nanocrystals were stable and dispersed in non-polar solvents such as toluene, chloroform, and THF, whereas the purified CdTe nanocrystals before the ligand exchange reaction were not redispersed in non-polar solvents. To our best knowledge, this is the first report for preparation of such stable, monolayer-protected CdTe nanocrystals with high QY at red spectral region.

SESSION CC8: Nanoparticles and Biomolecules

Chair: Andrew Taton
Tuesday Afternoon, November 29, 2005
Room 300 (Hynes)

3:30 PM *CC8.1

Conjugation of nanoparticles with proteins and DNA: Study of the biomolecular conformation. Kimberly Hamad-Schifferli, Mechanical and Biological Engineering, MIT, Cambridge, Massachusetts.

Nanoparticles have found a wide variety of uses in biological applications, such as sensors, drug delivery, and imaging. Conjugation of nanoparticles to biomolecules can now be routinely achieved by a broad range of methods. However, in all of these applications it is crucial that the structure of the DNA and protein retain its functional form. This can be quite challenging for proteins, which have a complex three-dimensional structure but also a number of amino acids that can non-specifically interact with nanoparticle surfaces. We investigate the structure of simple proteins and DNA covalently bound to metal nanoparticles at a specific site on the biomolecule. We probe how it is influenced by nanoparticle ligand, size, and chemical treatment by using biophysical characterization techniques.

4:00 PM *CC8.2

Nanoparticles: Scaffolds for Biomacromolecule Surface Recognition. Vincent Rotello, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts.

Metal, metal oxide and semiconductor nanoparticles provide useful scaffolds for creating receptors targeted at the surfaces of biomacromolecules. In our research, we are combining synthesis, materials science, and biology to create nanoparticles that bind to proteins, nucleic acids, and polysaccharides. The use of nanoparticles to create new systems for chemotherapeutics and diagnostics will be discussed. These studies use two unique attributes of nanoparticles: 1) Nanoparticles can be imprinted with target molecules, providing a means for enhancing specificity 2) Particles have sizes commensurate with proteins, giving them surface areas well-suited to binding of protein and DNA surfaces.

4:30 PM *CC8.3

Peptide Mediated Nanoparticle Assembly. Molly Stevens, Materials, Imperial College London, London, United Kingdom.

The ability to direct the assembly of inorganic nanoparticles has received growing interest in the creation of new nanotechnology devices. The development of new methods to control nanoparticle assembly may also impact on certain applications in medical science such as the generation of novel tunable and/or switchable materials. In particular, the ability to dynamically assemble and disassemble such structures under physiological conditions would be valuable for materials to be used in sensing and drug delivery. Here I will discuss peptide mediated assembly of nanostructures and demonstrate control over the assembly/disassembly process under physiologically relevant conditions (pH, temperature) as well as light-activated assembly/disassembly.

SESSION CC9: Nanotubes I

Wednesday Morning, November 30, 2005
Room 300 (Hynes)

8:30 AM *CC9.1

DNA-wrapped Carbon Nanotubes: From Separation to Assembly. Ming Zheng, DuPont Central Research and Development, Wilmington, Delaware.

Single-stranded DNA (ssDNA) forms stable complex with carbon nanotube (CNT) and effectively disperses CNT into aqueous solution. Separation and purification of CNTs with well-defined chirality and length can be achieved with DNA-wrapped carbon nanotubes. In this talk, I will present our latest CNT separation results, and describe a spontaneous DNA-CNT alignment phenomenon at the liquid/solid interface.

9:00 AM CC9.2

An Optical Study of Phonon-Assisted Excitonic Processes for a (6,5) Enriched DNA-wrapped Single Walled Carbon Nanotubes Sample. Shin Grace Chou[1], Matthew F. Decamp[1], Georgii Samsonidze[2], J. Jiang[3], Eduardo B. Barros[4], Flavio Plentz[5], Ado Jorio[5], Ming Zheng[6], G. Bibiana Onoa[6], Ellen D. Semke[6], Andrei Tokmakoff[1], Riichiro Saito[3], Gene Dresselhaus[7] and Mildred S. Dresselhaus[2,8]; [1]Chemistry, MIT, Cambridge, Massachusetts; [2]EECS, MIT, Cambridge, Massachusetts; [3]Physics, Tohoku University, Sendai, Japan; [4]Physics, UFC, Fortaleza, CE, Brazil; [5]Physics, UFMG, Belo Horizonte, MG, Brazil; [6]Central Research and Development, Experimental Station, Dupont, Wilmington, Delaware; [7]Francis Bitter Magnet Laboratory, MIT, Cambridge, Massachusetts; [8]Physics, MIT, Cambridge, Massachusetts.

A (6,5)-enriched DNA-wrapped single walled carbon nanotube (SWNT) hybrid sample, that was separated using ion exchange chromatography, was studied using different optical characterization techniques. The photoluminescence emissions observed at special excitation energy values were identified with specific mechanisms of phonon-assisted excitonic absorption and recombination processes associated with (6,5) nanotubes. In addition, a series of non-degenerate pump-probe measurements were carried out on the (6,5)-enriched DNA-wrapped SWNT sample to further understanding the dynamics of the phonon-assisted excitonic processes. By keeping the pump energy constant and systematically varying the values of the Eprobe to be in and out of resonance with both the majority (6,5) and the minority (n,m) SWNT species in the sample at different pump fluence levels, a decay component associated with a hot phonon-absorption process is studied in detail. The experimental results give insights into the more detailed phonon-assisted non-radiative relaxation processes in the exciton generation and depletion events, with possible mechanisms involving both bright and dark excitonic states. The clear observation of such detailed phonon-assisted processes is aided by having a highly (6,5) enriched SWNTs sample wrapped in DNA and the high concentration of specific hot phonons states associated with a one dimensional system. Similar phonon-assisted processes are not separately identified in bulk semiconductor materials. The MIT authors acknowledge support under Dupont-MIT Alliance, NSF Grants DMR 04-05538, DOE Grant DEFG02-99ER14988, and INT 00-00408. The Brazilian authors acknowledge support from the Instituto de Nanosciencias, Brazil. R.S. acknowledges a Grant-in-Aid (No. 16076201) from the Ministry of Education, Japan.

9:15 AM CC9.3
Bromine-Functionalized Transparent Carbon Nanotube Thin Films as Electronic Grade Materials. Giovanni Fanchini, H. Emrah Unalan and Manish Chhowalla; Materials Science and Engineering, Rutgers University, Piscataway, New Jersey.

The uniform deposition of transparent thin films of singly-walled carbon nanotubes (SWNTs) has opened new possibilities for their use in electronic applications, especially as transparent thin film transistors [1]. However, there is little work on doping and functionalization of such thin films, even if functionalization is widely accepted to be a route to improve the SWNT properties. For example, functionalization could lead to n-type doping, as is the case with bromine [2]. In this work, we will report on the preparation of Br-functionalized thin films from purified and shortened HipCoTM SWNTs treated in phosphorus tribromide (PBr3). Brominated nanotubes were subsequently suspended in water, filtered and deposited on to different substrates (glass, Si and SiO2 on Si) and used as active layers in thin film transistors. Ab-initio simulations [3] were used to model and optimize the doping process. The density of the films is controlled by changing the concentration of SWNTs in the suspension (0.5-60 mg/l). Characterization by electron microscopy, X-ray fluorescence, UV-visible, IR and multi-wavelength Raman spectroscopy has been used to verify the incorporation of Br and investigate the nature and the location of the functionals, also in comparison with the ab-initio simulations. Electrical properties and comparison of brominated and non-brominated transparent nanotube thin film transistors will be presented and discussed in detail. [1] Z. Wu et al, Science, 305 (2004) 1273 [2] A.M. Rao et al, Nature, 388 (1997) 257 [3] Gaussian03TM, Revision C.02, M.J. Frisch et al, Gaussian Inc., Wallingford CT, 2004

9:30 AM CC9.4
Observation of structure-dependent radial breathing mode Raman cross-section of single-wall carbon nanotubes. Zhengtang Luo[1], Stephens K. Doorn[2] and Fotios Papadimitrakopoulos[1,3]; [1]Polymer Program, Institute of Materials science, University of Connecticut, Storrs, Connecticut; [2]Chemistry Division, Analytical Chemistry Science, Los Alamos National Laboratory, Los Alamos, New Mexico; [3]Department of Chemistry, University of Connecticut, Storrs, Connecticut.

Aqueous dispersed individual single-walled carbon nanotubes suspended in sodium sodecyl sulfate was interrogated with excitation wavelengths every 2 to 5 nm between 695 and 985 nm. The resonance Raman profiles of the radial breathing mode (RBM) of HiPco single walled carbon nanotubes (SWNTs) was fitted to extract the optical transition energies, as well its full-width at half-max (FWHM), and the Raman cross sections. Significant agreement between the photoluminescence and Raman results was found. However, the Raman cross section is highly dependent on the family of SWNT, in which for mod(n,m,3)=1 semi-conducting nanotubes are considerable lower than the mod(n,m,3)=2 counterparts. Raman cross sections are also found to be heavily dependent on the tube chirality. This provides a new methodology to discriminate SWNTs with similar diameter, yet different chiral angle, by resonance Raman spectroscopy. Moreover, the empirical Raman cross-sections provided herein, can be used to accurately determine both diameter and chirality (n,m) distribution of nanotubes in a given sample.

9:45 AM CC9.5
Functionalization of Single Walled Carbon Nanotubes using Organic Dyes. Madhuvanthi Agaram Kandadai[1], Donghui Zhang[2,3], Aditya Avadhanula[1] and Seamus Curran[3]; [1]Chemical Engineering, New Mexico State University, Las Cruces, New Mexico; [2]Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico; [3]Physics, New Mexico State University, Las Cruces, New Mexico.

Single walled carbon nanotubes (SWNT) exhibit many unique properties such as high electrical and thermal conductivity, high tensile strength and good thermal stability. However, integration of SWNT into devices or other existing technologies are a relatively new endeavor. In order to maximize the effect of SWNT and achieve best overall performance of devices, it is important to have a good interfacial interaction between SWNT and other components within the devices. Chemical modification of SWNT surface is the most obvious approach. In this paper we report a method of covalently linking dye molecule (EOSIN Y) with acid treated SWNTs through a linker molecule (ethylene diamine). The reaction product was characterized using Raman spectroscopy as well as atomic force microscopy (AFM) and scanning electron microscopy (SEM). This novel dye/SWNT composite can potentially be used in solar energy harvesters as the dye is a good chromophore and the carbon tubes can contribute to both charge separation as well as electron transfer.

SESSION CC10: Nanotubes II
Chair: Nicola Marzari
Wednesday Morning, November 30, 2005
Room 300 (Hynes)

10:30 AM *CC10.1
Near-infrared Fluorescence Microscopy and Spectroscopy of Single-Walled Carbon Nanotubes in Biological Environments. Paul Cherukuri, Tonya K. Leeuw, Sergei M. Bachilo and R. Bruce Weisman; Dept. of Chemistry, Rice University, Houston, Texas.

Before the remarkable properties of single-walled carbon nanotubes (SWNT) can be harnessed for biological and medical applications, a wide range of studies must be performed to explore interactions between nanotubes and biological systems. One serious obstacle to such research is the difficulty of detecting carbon nanotubes in complex biological environments. We report here the development of near-infrared fluorescence techniques as a powerful new tool for this purpose. Our methods exploit the discovery of band-gap photoluminescence from pristine SWNT at wavelengths between 900 to 1600 nm. Using visible diode lasers for excitation, InGaAs arrays for detection, and spectral filtering to restrict detection to wavelengths beyond 1100 nm, we have been able to detect and quantify low concentrations of SWNT in biological cells, tissues, and organisms. Although SWNT have small quantum yields of emission, they can still be detected with high contrast because they show no photobleaching or blinking, and their biological surroundings emit only negligible endogenous fluorescence at the long wavelengths of observation. We have also modified an optical microscope for near-infrared fluorescence imaging beyond 1100 nm and have used the instrument to acquire biologically informative micrographs showing SWNT inside macrophage cells that had been incubated in growth medium containing nanotubes. These nanotubes had been ingested by an active process deduced to be phagocytosis and were found to be localized inside the cells, apparently in phagosomes. Further results will be reported on the preparation of aqueous SWNT suspensions using natural biological polymers in place of synthetic surfactants or polymers, as an important step in the investigation of nanotube toxicity and biodistribution patterns.

11:00 AM CC10.2
Rectifying Diodes from Asymmetrically Functionalized Single Wall Carbon Nanotubes. Zhong Wei, Mykola Kondratenko, Le H. Dao and Dmitrii F. Perepichka; Energy, Materials and Telecommunications, INRS - University of Quebec, Varennes, Quebec, Canada.

Although a number of different functionalization strategies have been reported for SWNTs, the selectivity was limited to walls or both ends of the tube. The resulting modified nanotubes have not been investigated as electronic devices with tailored electronic properties. We have recently succeeded in preparation of asymmetrically functionalized single-wall carbon nanotubes (SWNT) have been prepared via a covalent reaction of 11-mercaptoundecanol modified Au surface with oxidized SWNT cylinders. While one end of the tubes is attached to gold substrate via ester groups, the free carboxylic substituents on the other end can be either ionized (CO2-) or esterified (CO2Et), creating a donor-acceptor asymmetric and acceptor-acceptor symmetric SWNT, respectively. Study of the SWNT monolayer conductance in Hg drop junction experiments reveals a pronounced diode-like behavior for donor-SWNT-acceptor junctions, while acceptor-SWNT-acceptor junctions are electrically symmetric.

11:15 AM CC10.3

Resonance Raman Study Of The Effects Of DNA-Wrapping Agents on Single Walled Carbon Nanotubes.

Shin Grace Chou[1], H. Son[2], Aurea Zare[2], Georgii G. Samsinidze[2], Ado Jorio[3], Marcos Pimenta[3], Ming Zheng[4], G. Bibiana Onoa[4], E. D. Semke[4], Yan Yin[5], Andrew Walsh[5], Anna K. Swan[6], B. Goldberg[5,6] and S. M. Unlu[6]; [1]Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]EECS, MIT, Cambridge, Massachusetts; [3]Physics, UFMG, Helo Horizonte, MG, Brazil; [4]Central Research and Development, Experimental Station, Dupont, Wilmington, Delaware; [5]Physics, Boston University, Boston, Massachusetts; [6]ECE, Boston University, Boston, Massachusetts.

In this study, we use resonance Raman spectroscopy to study single walled carbon nanotubes (SWNTs) produced by the CoMoCAT method, wrapped with single stranded DNA. The DNA-wrapped CoMoCAT SWNTs are excited using a large number of discrete laser excitations, covering a nearly continuous energy range in the visible and near infrared. Both the DNA-wrapped and the as-produced CoMoCAT SWNTs (without DNA-wrapping) samples were studied in bulk and at the single nanotube level on a sapphire substrate. The DNA wrapping agent was found not only to change the interband transition energy, but the additional strain introduced by the wrapping agents is also found to shift the phonon frequencies for both the dispersive and non-dispersive Raman features in the range 1650-2100 cm-1, where second order and overtone modes for carbon nanotubes occur. The experiments were found to be in good agreement with the theoretically predicted phonon dispersion for the combination and overtone modes. The information provided by a nearly tunable laser system for characterization of the effects of DNA-wrapping on the CoMoCAT SWNTs sample is discussed. The MIT and BU authors acknowledge support from the Dupont-MIT alliance, NSF04-05538, and NIRT ECS-0210752. The Brazilian authors acknowledge support from FAPEMIG, FINEP, and Instituto de Nanosciencias, Brazil.

11:30 AM CC10.4

Theoretical and experimental studies of methyl radical on FeO(001), alpha-Fe2O3(0001) and Fe3O4(111) surfaces.

Jiang J. Jin[1], Xiaoyang Ma[2,3], Lin Liu[2,3], Peter Stair[2,3], Donald E. Ellis[1,2,3]; [1]Physics and Astronoomy, Northwestern University, Evanston, IL; [2]Chemistry Department, Northwestern University, Evanston, IL; [3]Institute for Environmental Catalysis, Northwestern University, Evanston, IL.

Adsorption of methyl radicals on iron oxide surfaces can be viewed as a starting point for understanding more complex organic molecule interactions with such surfaces. Here we report experimental and theoretical studies of adsorption of methyl on several iron oxide surfaces, using a novel source of the CH3 radical, thermally programmed desorption spectroscopy (TPD), Auger Electron Spectroscopy (AES), low-energy electron diffraction (LEED) and Density Functional Theory (DFT). DFT band structure and embedded cluster methods are used to characterize adsorption geometry, binding energy, vibrational spectra, and chemical bonding. Idealized and defected surfaces are examined in an effort to reconcile differences between theoretical predictions and observations.

11:45 AM CC10.5

Engineering the electronic structure and transport properties of carbon nanotubes via sidewall chemical functionalizations: a first-principles approach.

Young-Su Lee and Nicola Marzari; Department of Materials Science and Engineering and Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We have combined large-scale, Γ-point electronic-structure calculations with the maximally-localized Wannier functions approach in a novel method that allows to calculate efficiently and inexpensively the electronic structure and the quantum conductance of complex systems containing thousands of atoms. Our approach relies on the ability to map Bloch orbitals into maximally-localized orbitals, providing a minimal tight-binding Hamiltonian that preserves the full accuracy of the ab-initio calculations. This approach allowed us to characterize the effects of covalent functionalizations on the electronic transport properties of carbon nanotubes tens of nanometers long. We found that binding of aryl moieties or even atomic hydrogen to sidewall carbons induces sp^2 to sp^3 rehybridization, rapidly destroying the original π-electron manifold of the pristine metallic tubes. The band structure and transport properties are much less dependent on the chemical nature of the electropositive or electronegative residues of the organic ligands, than on the pattern and topology of the sp^3 rehybridizations. On the other hand, cycloaddition of nitrenes or carbenes is able to recover the sp^2 character of the sidewall carbons, whenever cleaving of the bond between backbone atoms is induced. A much weaker perturbation and scattering from the ligands thus ensues, preserving the unique electronic properties of the metallic graphitic manifold. We explore the tunability of the bond opening and closing mechanisms, that could have a profound effect on the electronic transport properties of nanotubes.

SESSION CC11:Assembly of Particles
Chair: Prashant Kamat
Wednesday Afternoon, November 30, 2005
Room 300 (Hynes)

1:30 PM CC11.1

Composite Photocatalyst Based on Nanofibers Containing Titanium Dioxide and Carbon Nanotubes.

Shahar Kedem, Dimitry Rozen, Yachin Cohen and Yaron Paz; Chemical Engineering, Technion, Haifa, Israel.

The electrospinning technique was used to fabricate composite polymer nanofibers that contained both TiO2 nanoparticles and Multi Wall Carbon Nanotubes (MWCNT). Fourier Transform Infra-Red (FTIR) spectroscopy was used to measure the UV-induced self-degradation rates of the fibers as well as the photodegradation rates of two model contaminants: acetone and carbon tetrachloride. A dramatic reduction in the UV-induced degradation rate of the nanofibers was observed in CNT-containing fibers. This stabilization phenomenon was corroborated by TEM micrographs of irradiated fibers, showing little or no damage by TiO2 to fibers containing CNTs. Photodegradation kinetics measurements of both contaminants showed that this increased stabilization by the presence of CNTs did not have a negative effect on the ability of the composite fibers to photodegrade acetone or carbon-tetrachloride. In fact, the photodegradation rate of CCl4 was higher by 33% in the presence of CNTs, and that of acetone by 10%. The origins of these phenomena will be discussed.

1:45 PM CC11.2

Interplasmon Coupling in Silver and Gold Nanorods.

K. George Thomas[1,2] and Prashant V. Kamat[2]; [1]Photosciences and Photonics, Regional Research Laboratory (CSIR), Trivandrum, India; [2]Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.

Anisotropic features of Au nanorods allow their orientation in lateral or axial fashion resulting in interplasmon coupling.[1,2) The possibility of using Au nanorod based assays for the detection of target molecules through their regiospecific modification was earlier proposed by invoking a simple quasistatic treatment for the nanorod-nanorod plasmon resonance spectra at different distances/orientations.[1a] Recently we have experimentally verified the interplasmon coupling in Ag nanorods and Au nanorods by interconnecting them using various bifunctional molecules (thioalkyl carboxylic acids, dithiols etc).[2a] Longitudinal self assembly of Au nanorods initially to dimers and further to linear assemblies through cooperative hydrogen bonding, allow unidirectional plasmon coupling. Also we have demonstrated the possibility of using nanorods for the selective detection of biologically important molecules.[2b] We could selectively detect micromolar concentrations of cysteine/glutathione from a pool of α-amino acids which makes Au nanorods versatile for sensing biologically important molecular systems bearing thiol and zwitterionic groups. This talk will highlight our recent efforts to (i) understand the interfacial properties of metal nanorods (ii) integrate nanorods into higher order assemblies using bifunctional molecules, and (iii) utilization of these nanohybrid systems as sensors of biologically important molecules. REFERENCES [1] (a) M. Gluodenis and C. A. Foss, J. Phys. Chem. B, 106, 9484 (2002); (b) K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, J. Phys. Chem. B, 107, 668 (2003) (c) K. K. Caswell, J. N. Wilson, U. H. F. Bunz, and C. J. Murphy, J. Am. Chem. Soc. 125, 13914 (2003). [2] (a) K. G. Thomas, S. Barazzouk, B. I. Ipe, S. T. S. Joseph and P. V. Kamat, J. Phys. Chem. B 108 13066 (2004); (b) P. K. Sudeep, S. T. S. Joseph and K. G. Thomas, J. Am. Chem. Soc. 127, 6517 (2005)

2:00 PM CC11.3

Organic Chromophores Self-Assembled on Mixed-Ligand Protected Nanoparticles.

Osman M. Bakr[1,2], Alicia M. Jackson[1], Benjamin H. Wunsch[1] and Francesco Stellacci[1]; [1]Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts.

Light harvesting antennas hold the key to progress towards efficient organic solar cells. Antennas must be able absorb on a wide spectral window that covers a significant portion of the optical spectrum. Relying merely on the intrinsic optical and photophysical properties of the dye-building blocks of the antenna will limit the efficiency of the antenna and choice of usable dyes. The use of exotic, as well as expensive, dyes can be avoided by exploiting the antenna's architecture. The optical and photophysical properties of a chromophore in an antenna can be controlled through tuning its interactions with other chromophores in the antenna. For example, the antennas of photosynthetic units in plants and bacteria are composed of many chromophores arranged in specific geometries that effectively use molecular architectures to achieve unparalleled efficiencies. Self-assembled monolayers (SAMs) of dyes on the surface of nanoparticles offer a promising route to constructing light harvesting antennas, because the possibility of tuning the intermolecular interactions between the dyes, by controlling, with nanometer scale precision, parameters like molecular spacing and orientation. In particular by using nanoparticles coated with a mixture of ligands it is possible to control molecular arrangements and environments. In this work the optical and photophysical properties of porphyrin SAMs assembled on Au and Ag nanoparticles are studied. We find that these properties significantly differ depending on the size and composition of the nanoparticle. The presence of a second, optically inactive, type of molecules in the ligand shell also plays an important role in determining the particle's optical properties. Our results indicate that the properties of chromophoric SAMs on nanopartcles depend not only on the optical properties of the metal cluster, but also on the conformation of the chromophores assembled on the metal cluster.

2:15 PM CC11.4
Directed Assembly of Ligand-Coated Gold Nanoparticles on Surfaces Patterned with Dip Pen Nanolithography.

Robert John Barsotti and Francesco Stellacci; Materials Science and Engineering, M.I.T., Cambridge, Massachusetts.

Understanding the unique electrical and optical properties of ligand-coated gold nanoparticles requires the ability to direct their assembly into specific patterns on predetermined locations on a substrate. Here we show that nanoparticle features can be fabricated using molecular recognition mechanisms, where molecules patterned onto a surface attract and bond to the molecular coating of monolayer protected metal nanoparticles. Dip Pen Nanolithography (DPN) was used to pattern surfaces with self-assembled monolayers (SAMs) composed of molecules terminated with specific functional head groups. The patterned surfaces, when immersed in a solution containing gold-nanoparticles (3 nm diameter) coated with molecules terminated with 'complementary' functional head groups, chemically direct the self-assembly of the nanoparticle patterns. Sub-80 nm features fabricated using both ionic and covalent bonds will be presented. Strategies to obtain single monolayers of nanoparticles on the molecular patterns and to prevent particle non-specific adhesion onto non-patterned regions of the sample will be discussed. We have found that substrate immersion time and nanoparticle concentration are the key parameters that play a role to achieve reliable and reproducible assembly of particle features. In particular we find that these parameters need to be varied when the bonding chemistry is altered but also when the particle size varies. We will also carefully compare various molecular linking approaches.

SESSION CC12: Photophysical Properties
Chair: Ming Zheng
Wednesday Afternoon, November 30, 2005
Room 300 (Hynes)

3:30 PM *CC12.1
On Route to Functional Materials Via Self-Assembly Imprinting of Bulk Silica Using Nanoparticle Templates.

Alexander Katz, Chemical Engineering, UC Berkeley, Berkeley, California.

The goal of bulk silica imprinting is the organization of chemical functional groups within pockets of controlled size and shape. These groups can subsequently be used as anchors for the confinement and organization of functional elements such as photoluminescent organic dye molecules in materials. The dye-containing imprinted materials may have perturbed and interesting photoluminescent properties relative to free dye in isotropic solution, as a direct result of the preferential dye molecule organization. We describe the design, synthesis, and characterization of mesoscale, bulk imprinted silica using a gold-silica core-shell nanoparticle as imprint species. Our objective is to use citrate-stabilized colloidal gold ($\sim$10 nm) as a template for the organization of thiol and amine functional groups via self-assembly in bulk silica. We have successfully synthesized materials consisting of over 30% by weight gold in silica via a novel sol-gel route relying on condensation of hybrid organic-inorganic core-shell nanoparticles at controlled pH. These materials consist of a porous silicate framework that allows for the removal of the gold templates via etching to leave behind functional group organization created by the imprinting process as well as the synthesis of imprinted pockets surrounding these organized functional groups. We describe the spectroscopic characterization of materials before and after gold removal, demonstrating gold nanoparticle isolation even at the high gold loadings used. This isolation is a direct result of the core-shell architecture of the nanoparticle imprint. Efforts for imprinting thiol functional groups by employing the strong interaction between thiols and gold within the context of our materials synthesis approach are described. To this end, we have synthesized and characterized gold-silica core-shell nanoparticles consisting of a mercaptosilane core-shell interface. We have characterized this interface using steady-state fluorescence on pyrene-containing probe molecules, which exhibit significant amplification of the pyrene fluorescence emission intensity upon binding to the gold nanoparticle surface. Future directions for employing these thiolate-containing nanoparticles as imprints in our materials synthesis strategy are described.

4:00 PM CC12.2
Supramolecular Organization in Ultra-Thin Films of alpha-Sexithiophene on Silicon Dioxide.

Michele Muccini, Maria Antonietta Loi, Enrico Da Como, Franco Dinelli, Fabio Biscarini, Mauro Murgia and Roberto Zamboni; Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche, Bologna, Italy.

The supramolecular organization of organic semiconductors on the dielectric layer of thin film field-effect transistors is a crucial factor in achieving good device performance. Charge transport in these devices occurs near the interface with the gate dielectric. By confocal laser scanning microscopy (CLSM) and photoluminescence (PL) spectroscopy we study the supramolecular organization in ultra-thin films of a prototype organic semiconductor, a-sexithiophene, on silicon dioxide, a widely used transistor gate dielectric. We demonstrate that in submonolayer films of sexithiophene (T6), regions where the molecules stand on their long molecular axis coexist with regions where the molecules lie flat on the substrate [1]. When the first monolayer is completed, all T6 molecules stand on the substrate, and the flat molecules detected in the submonolayer films are no longer present. Spatially-resolved spectroscopy evidences that in films thicker than two monolayers standing molecules show H-like aggregation as in the single crystal. The PL of molecules with the long molecular axis parallel to the substrate reveals the formation of J-like aggregates. These observations show how it is possible to control the nature of intermolecular interactions and tune the solid-state optical properties. Finally, we demonstrate that CLSM and spatially-resolved PL spectroscopy provide unprecedented insights in the molecular organization of organic thin films. [1] M. A. Loi, E. Da Como, F. Dinelli, M. Murgia, R. Zamboni, F. Biscarini and M. Muccini, Nature Materials 4, 81 (2005).

4:15 PM CC12.3
Energy modulated heterostructures for charge transfer and confinement based on conjugated polymers.

Francisco Gontijo Guimaraes, Higor Rogerio Favarim, Valtencir Zucolloto and Osvaldo Novais Oliveira; Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, Sao Paulo, Brazil.

It is demonstrated that multilayer structures with modulated band gaps can be used for efficient charge transfer and carrier confinement inside of a light emitting polymer sample. The films were produced with the layer-by-layer technique (LBL) with a poly(p-phenylene vinylene) (PPV) precursor and a long chain dodecylbenzenesulfonate ion (DBS). DBS is incorporated selectively into the precursor chain, and with a rapid, low temperature conversion process (100oC) superstructures with variable HOMO-LUMO gap can be formed along the deposition direction by changing the DBS concentration. Structures with different stair-type energy modulations were produced, which are thermally stable and reproducible, as demonstrated by UV-VIVS absorption measurements. Energy differences of up to 0.5 eV between the lowest and highest conjugated layers inside the stair structure could be achieved. Photoluminescence measurements show that this energy separation is sufficient to produce an efficient charge transfer via Foerster processes from the highest energy to the lowest band gap stair. Structures with 2 bilayers of PPV-DBS per stair display higher emission intensities compared to an equivalent highly conjugated PPV layer, demonstrating that emission can be improved in organic semiconductors by carrier confinement in a very thin layer. An acceptor layer based on an azochromophore, separated by an optically inert spacer from the stair structure, was also used to probe the strength and the range of transfer process inside the energy modulated structures. These multilayer films, controlled at the nanometer level, can be used to enhance various organic optoelectronic and photovoltaic devices.

4:30 PM CC12.4
Monolayer Assembly of J-aggregates at Air-Water Interface Using Cyanine Dyes Free of Hydrophobic Long Alkyl Chains.

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We present a new approach to Langmuir Blodgett (LB) assembly and apply it to forming polycrystalline monolayers of J-aggregated cyanine dye at the air-water interface. In contrast to earlier works, in which dye molecules are functionalized with long alkyl (e.g. hexadecyl or octadecyl) chains to render them insoluble in the water subphase, in this technique long alkyl chains are absent and the dye itself functions as the amphiphile. Multilayer films of dye assembled by alkyl chain free assembly (ACFA) are up to 4 times more concentrated, as compared to previous growth methods. The collective absorption band of the resulting J-aggregate crystalline films is of narrower linewidth, indicating a greater degree of exciton delocalization. Crystallites of J-aggregated cyanine dyes are known to exhibit a very high oscillator strength collective optical transition, which is dependent on the packing density and molecular arrangement of the dye species. We therefore demonstrate that ACFA allows us to control whether the dye is aligned flat or on-edge relative to the air-water interface, which we characterize with optical spectroscopy and surface tension measurements. We make direct comparison between ACFA and the standard LB alkyl functionalized approach for the dye 1,3,1',3'-tetraethyl-5,6,5',6'-tetrachloro-2,2'-imidacarbo-cyanine chloride (TTBC). We also form multilayers of 2,2'-dimethyl-8-phenyl-5,6,5',6'-dibenzothiacarbocyanine chloride, a dye that previously had only been assembled via co-spreading of fatty acids and show that the ACFA multilayer films posses higher dye concentrations. Our work demonstrates that ACFA is quite general in that it can be used to form polycrystalline J-aggregate thin films for dye molecules that in prior works only showed J-aggregation in solution. We use ACFA to insert a thin film of J-aggregates inside an optical microcavity and observe exciton-polariton spectral peaks, a signature of room temperature strong coupling phenomena characteristic of strongly absorptive organic structures [Tischler, Bradley, Bulovi?, Song, Nurmikko, Physical Review Letters, 2005]. The ACFA synthetic step is a significant milestone in the development of thin film systems that exhibit strong coupling of light and matter, an enabler of room temperature single photon optics and optoelectronic devices that operate in the strong coupling regime.

4:45 PM CC12.5

Computer simulation of the light-induced trans-cis isomerization of azobenzene grafted onto montmorillonite sheets.

Hendrik Heinz, Richard A. Vaia and Barry L. Farmer; Materials and Manufacturing Directorate, Polymer Branch, Wright Patterson AFB, WPAFB, Ohio.

Novel photoresponsive materials with switchable gallery spacing between layered silicate sheets would provide an important mechanism for actuator or sensor applications. Molecular dynamics simulation has been shown to be a useful tool in predicting such basal plane spacings [1] and allows to investigate photochemical trans-cis isomerizations, which typically occur on a time scale of picoseconds. We employ the polymer consistent force field with recent extensions for quantitative reproduction of interface energies. The photoisomerization is accomplished in the course of the simulation through stepwise modification of the (classical) C-N=N-C torsional potential and sufficient pre- and post-equilibration time. Different systems are then investigated on the montmorillonite surface, with different cation exchange capacity and degree of ion exchange: 4-(6-ammonium-n-hexyl)-azobenzene ions, 4-ammonium-azobenzene ions, and 4,4'-diammonium-azobenzene ions grafted to the silicate surface. Typical structures are monolayers between the two surfaces, an azobenzene bilayer, and an azobenzene monolayer tethered to both surfaces. During the photoreaction, alkyl chains in the first system act as flexible spacers and accommodate the azobenzene unit in both configurations without significant changes in gallery spacing, in agreement with previous experimental observations [2]. However, the inclination angle of the benzene rings relative to the surface increases in the cis form. 4-ammonium-azobenzene ions are more rigid and show a noticeable reponse with regard to basal plane spacing. 4,4'-diammonium-azobenzene ions are simultaneously bonded to the upper and lower silicate sheet and stand upright to the silicate surface, which is reinforced through hydrogen bonds to the surface oxygen. They yield a reversible 15% reduction in basal plane spacing (+/-3 Angstroms) upon trans-cis conversion. As a result, rigid, pillar-like structures between the clay sheets show the strongest response to a laser pulse with regard to controllable switching of the gallery height and might be suited for applications in bistable actuators. [1] Heinz, H.; Suter, U. W. Angew. Chem. Int. Ed. 2004, 43, 2239-2243. [2] Ogawa, M.; Ishii, T.; Miyamoto, N.; Kuroda, K. Adv. Mater. 2001, 13, 1107-1109.

SESSION CC13: Theory on Nanoparticles 1

Chair: David Norris
Thursday Morning, December 1, 2005
Room 300 (Hynes)

8:30 AM CC13.1

Raman Spectroscopy on Micromachining and Microindentation on Carbon Nanotubes in a Composite.

Ayman Bassil[1], Pascal Puech[1], Paulo S. Pizani[2], Renato G. Jasinevicius[5], Emmanuel Flahaut[4], Sophie Barrau[3], Philippe Demont[3], Colette Lacabanne[3] and Wolfgang Bacsa[1]; [1]LPST, UPS, Toulouse, France; [2]Departamento de Fisica,, UFSCAR, Sao-Carlos, Brazil; [3]LPP, CIRIMAT, UPS, Toulouse, France; [4]LCMIE, CIRIMAT, UPS, Toulouse, France; [5]Departamento de Engenharia Mecanica, USP, Sao Carlos, Brazil.

Indentation is currently used to characterize the structural and mechanical properties of materials. The combination of indentation tests with Raman micro-spectroscopy provides a powerful and rapid tool for monitoring pressure-induced phase transformations in hard materials such as ceramics and semiconductors. Here we present first results on Vickers micro indentation and micro machining by using single point diamond turning on composite of carbon nanotubes into an epoxy resin (CNT-ER). Samples with different loads were studied, in which the Raman spectrum was performed always at the center of the imprint. The results show that the indentations lead to a structural disorder and to compressive residual stresses. These results are compared with those obtained by applying hydrostatic and non-hydrostatic pressure on double walled carbon nanotubes. Also, we analyze and discuss results of cyclic indentations on these polymers (CNT-ER) and highly ordered pyrolytic graphite (HOPG). Furthermore, the AFM results show that the machined surface is not so damaged compared to the non machine one, indicating that this process can be used to perform special surface forms in these materials.

8:45 AM CC13.2

Photoinducted Kinetics in Ag Nanoparticles Deposited on the Indium Tin Oxide Surface.

Kazimierz J. Plucinski[1], I. V. Kityk[3], J. Ebothe[2], G. Chang$^4 and M. Oyama^5$;[1]Electronics, Military University of Technology, Warsaw, Poland; [2]Physics Department, Univ. of Reims, Reims, France; [3]Institute of Physics, J. Dlugosz Univ., Czestochowa, Poland; [4]Department of Material Chemistry, Kyoto University, Kyoto, Japan; [5]International Innovation Center, Kyoto University.

Enhancement of the UV-visible optical absorption spectra for the Ag nanoparticles on Indium Tin Oxide Surfaces prepared by a seed-mediated growth technique was found. A Bicolor coherent beam of 18 ps pulsed Nd-YAG laser with wavelengths 1060 nm (as fundamental) and 530 nm (as frequency doubled ones) was used as photoinducing coherent beam. The maximum changes of optical density monitored by absorption were observed for surfaces with a low resistance (about 4 Ω). No noticeable change was observed with those of higher resistance (about 50 Ω). At the same time spectral positions of the absorption maximums at 440 nm were almost unchanged in both cases. This may be a consequence of interaction between the local bicolor coherent photoinduced static field during short time and the surface-plasmon polaritons interacting with the photoinduced phonons. Several contributions may give also grating created by a coherent bicolor light forming a superstructure typical for quantum crystals. The physical insight of the phenomenon observed is determined by a collective excitation of the Ag NP free plasmon-carriers. The SPR is a main factor favoring nonlinear optical susceptibilities, strictly related to dielectric confinement (i.e., of the local field effect) that determines the corresponding hyperpolarizabilities. However the inclusion of the nanoparticles to the dielectric matrices substantially restrains technological possibilities of using the optoelectronic properties, particularly for optoelectronic devices. From this point of view, the configuration of ITO attaching the nanoparticles seems to be more convenient technologically. The use of ITO electrodes may cause the principal difference in the behavior of the photokinetics due to the specific charge transfer in the ITO-metallic interfaces, as it was just shown during the manifestation of the photoinduced electrogyration effect. Among metallic nanoparticles, silver ones have attracted interest because their SPR energy are located far from the inter-band transition energy. So, during the description of the photoinduced effects, one can neglect the strong inter-band contributions and assume the predominant role of SPR contribution. At the same time using of coherent bicolor laser light may form local electrostatic field localized on the interface separating Ag NP-ITO. This field may operate by electron charge transfer features determining microscopic optical hyperpolarizabilities and macroscopic susceptibilities. Among the latter particularly important seems to be two-photon absorption susceptibility.

9:00 AM *CC13.3
First-principles engineering and characterization of functionalized nanotubes and nanoparticles. Nicola Marzari, [1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We studied the effects of covalent functionalizations on the electronic structure and quantum conductance of carbon nanotubes, using a novel approach based on maximally-localized Wannier functions to characterize nanostructures containing thousands of atoms while preserving full first-principles accuracy. It is found that binding of aryl moieties or even atomic hydrogen to sidewall carbons induces sp^2 to sp^3 rehybridization, rapidly destroying the original π manifold of pristine metallic tubes. The band structure and transport properties are also much more dependent on the pattern and topology of the sp^3 rehybridizations than on the chemical nature and electronegativity of the residues in the aryl moieties. On the other hand, cycloaddition of nitrenes or carbenes can induce cleaving of the bonds between backbone atoms, recovering to a large degree the sp^2 character of the sidewall carbons. A much weaker scattering from the ligands thus ensues, allowing to preserve or even control the conductance properties of the metallic graphitic manifold. A brief review will also be given on the role of ligands in determining plasticity and nucleation in semiconducting nanoparticles under pressure or during a shock wave.

9:30 AM *CC13.4
Exploiting anisotropy for patchy particle self-assembly. Sharon C. Glotzer, Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan.

The ligand coating on nanoparticles provides an important opportunity for imparting anisotropy to interparticle interactions. This anisotropy can lead to the self-assembly of particles into novel structures.

SESSION CC14: Theory on Nanoparticles 2
Chair: Sharon Glotzer
Thursday Morning, December 1, 2005
Room 300 (Hynes)

10:30 AM *CC14.1
Towards a Tetravalent Chemistry of Colloids. David R. Nelson, Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts.

Self-assembly and manipulation of micron scale colloidal particles have many potential uses, including particle based assays in biomedicine and photonic band gap materials. Dense colloid arrays (possibly involving DNA linker elements) usually display the high coordination numbers (Z =12-14) characteristic of an isotropic pair potential. It is therefore of some interest to devise a means by which micron scale colloids could link with, say, a four-fold valence, similar to the sp^3 hybridized chemical bonds on an Angstrom scale associated with, e.g., carbon, silicon and germanium. When rod-shaped gold particles, gemini lipids or triblock copolymers are used to coat spherical colloid particles (or liquid droplets), a 2D nematic phase can arise. This topology can lead to four disclination defects in the ground state, a circumstance which could allow creation of novel tetravalent colloidal materials with chemical linkers or DNA at the defect cores. When the nematic films are thick, there is a transition from a 4-fold to a 2-fold valence.

11:00 AM *CC14.2
Computational design of group IV nanostructures. Giulia Galli, Lawrence Livermore National Laboratory, Livermore, California.

Computational tools are playing an increasingly important role in understanding and controlling matter at the microscopic scale, by predicting with quantitative accuracy the property of materials based on their atomic and molecular constituents. In the next decade, the coming of age of first principles theories of matter and related computational techniques –as well as the growth of computer power– will allow one to simulate a wide variety of alternative materials with desired properties, and thus the engineering of optimized materials from first principles will become possible. In this talk, computer simulations using First Principles Molecular Dynamics (FPMD) and Quantum Monte Carlo (QMC) techniques are employed to solve specific nanoscience problems, in particular to investigate the physical properties of group IV semiconductor nanostructures and their possible use as chemical and biological labels. While robust experimental results have been established for II-VI nanocrystals in the last decade, group IV elemental nanostructures are much less well characterized. The interplay between quantum confinement effects and surface properties has not been fully understood, and the effects of preparation conditions on the physical properties of Group IV nanoparticles remain an open issue. Our simulations are aimed at understanding the physical and chemical properties of C, Si, SiC and Ge nanoparticles with diameters up to 2-3 nm. In particular, we will present investigations of optical gaps and surface properties, and simulations of the effect of different preparation conditions on the structure of Si nanoparticles. Recent simulation results on the early stages of quantum dot functionalization and on salvation properties will also be discussed.