SYMPOSIUM O
Nanoparticles and Nanostructures in Sensors and Catalysis

November 28 - December 2, 2005

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* Invited paper
8:15 AM O1.1
Strain Fields Generate Domain Boundaries in Carbon Nanotubes During Catalytic Synthesis.

Ex-situ transmission electron microscopy (TEM) was performed on catalytically-grown multi-wall carbon nanotubes. Two types of catalyst-nanotube-wall interfaces were identified - one characterized by a round particle closer to the nanotube root and by an elongated particle farther away from it. The nanotube exhibited two distinct types of boundaries between crystalline domains with different orientations - twinned boundaries in correspondence of spherical particles and tilt boundaries in correspondence of the elongated particles. TEM evidence suggests that the domain boundaries maintain a rather steady position coupled to the catalytic particles, while the carbon atoms pyrolyse along the nanotube axis away from the particles. From these considerations it is possible to conclude that the relative movement of the carbon atoms with respect to the dislocation lines comprising the nanotube domain boundary located at the catalyst-wall interface is a significant mechanism for nanotube crystal growth driven by surface diffusion (1). The results are interpreted in light of the concurrence of base- and tip-growth for the catalytic synthesis of nanotubes (2). This work was supported by Philip Morris USA Nanoscience and Engineering Initiative of the National Science Foundation under NSF Award No. DMR-0117702. References (1) O.A. Louchev, Y. Sato, H. Kanda (2002) Morphological characterization, evolution and opening closure during carbon nanotube growth mediated by surface diffusion. Physical Review E 66, 011601-17, (2) L.M. Dell’Acqua-Bellavitis, J.D. Ballard, P.M. Ajayan, R.W. Siegel (2004) Kinetics for the synthesis reaction of all single carbon nanotubes. A study based on in situ diffraction, Nano Letters 4, 1613-1620.

8:30 AM O1.2
2- and 3-Dimensional Metal Nanoparticle Catalyst Systems to Obtain High Reaction Selectivity. The Catalytic Nanodiode for Energy Conversion.
Gabor A. Somorjai 1,2, Xiao Zhong 1, Anthony Contreras 1,2 and Robert Rioux 1,2, Chemistry, University of California, Berkeley, Berkeley, California; 3Lawrence Berkeley National Laboratory, Berkeley, California.

The evolution of nanosciences provides opportunities and challenges for catalysis science and technologies in synthesis, characterization and reaction studies of catalyst nanostructures. Monodispersed platinum and rhodium nanoparticles of different shapes in the 1-10 nm range are synthesized by solution-based reduction methods. Particles are capped with a polymer that prevents their aggregation and allows them to form a flat outgrowth in mesoporous silica or alumina supports to produce 2-dimensional and 3-dimensional catalyst systems. The nanoparticle catalysts are characterized by a combination of techniques at each phase of preparation. The preparation of the polymer, reduction step, and the nanoparticle carried out as a function of size and shape of the metal particles and nature of the support. Hydrocarbon conversion reactions have been studied on platinum and carbon monoxide hydrogenation over rhodium nanoparticles. Using nanoscience catalyst design to obtain high selectivity catalyst systems is now possible. When exothermic catalytic reactions (H2/O2, CO/O2) are carried out over a platinum thin film (6-8 nm) deposited on a semiconductor (TiO2 or GaN Schottky barrier), steady state flux of electrons could be detected for hours at an electrode attached to the semiconductor. By simultaneously monitoring the electron flux and the reaction rates a maximum of 5 electrons for 4 product molecules could be detected. Hot electron data were collected on a ~20 femtosecond time scale during exothermic processes at metal surfaces, which is responsible for the lack of molecular excitations at the same surface that has much more electronics. The mean mean free path in the metal (~5-10 nm), the barrier height at the metal-semiconductor interface, and the thermal and chemical stability of the catalytic nanodiode control the electron flow.

9:00 AM O1.3
The Effect of Particle Charge on the Catalytic Properties of Nanostructured Metal Catalysts. Sergey Alexandrovich Gurievich 1, V. M. Kozevin 1, I. N. Yaasievich 1, D. A. Yasvis 1, T. N. Rostovtchikova 1 and V. V. Smirnov 2, 1Lofe Institute, St. Petersburg, Russia; 2Department of Chemistry, Moscow State University, Moscow, Russian Federation.

The catalyst structures, which are thin granulated films consisting of Cu, Ni, or Pd nanoparticles, were fabricated by means of laser electrodispersion technique. This technique allows producing nearly monodispersive and amorphous nanoparticle films (the mean particle sizes are 5.0 nm for Cu, 2.5 nm for Ni, and 2.0 nm for Pd; the size dispersion is less than 10%). These particles were deposited on dielectric (thermally oxidized silicon) or semiconductor (naturally oxidized Si) supports and the resulting particle surface density was closely controlled by the time of deposition. The most important common feature of the fabricated catalysts is their unusually high (up to 106 product mol/metal mol h) catalytic activity measured in several chlorohydrocarbon conversions (C5, Ni) and hydrosilation (Ni, Pd) reactions. In all the reactions, strong dependences of the specific catalytic activity on the particle surface density and solution polarity have been observed. The nature of the support affected the activity as well, for instance, different activities were measured when using p- or n-doped Si supports. These experimental facts are explained assuming that, alongside with the small size and amorphous state of the particles, particles charge fluctuations (resulting from interaction of particle or particle tunnel electron transfer) determine the catalytic activity of these structures. A theoretical model is developed providing a means for calculating the number of the charged particles in case when the structure is deposited on a dielectric or on a semiconductor support. The speculations on the mechanism of tunnel electron transfer from the charged nanoparticle to the chemisorbed reagent molecule show that, for the reactions proceeding with the electron transfer, nanoparticle charging may result in substantial reduction of the reaction activation energy. Combining these two models allows quantitative estimating the effect of the particle charge on the catalytic activity. Estimations made on this basis are in good agreement with the experimental results. Utilization of the described model (related to their charging) opens up a new way for managing the catalytic properties of immobilized metal nanoparticles.

9:15 AM O1.4

Nanocomposites of gold and anatase have been prepared by reactive thin film deposition using two magnetron sputter sources and metallic targets. The density, microstructure, and crystalinity of the titania films depends on the deposition angle, process gas pressure, and post-deposition anneal temperature. While dense films are achieved by normal sputter geometry, high surface area films composed of fibrous columns of anatase are achieved by orienting the substrate at a near glancing angle with respect to the titanium source. The gold content of co-deposited films can be varied over a wide range by controlling the relative deposition rates. Films several micrometers thick are readily achieved by limiting the O2/Ar ratio in the process gas to maintain a high deposition rate. The high surface area columnar films containing gold are observed to be catalytic for CO oxidation at room temperature. An infrared gas cell has been used as a reaction cell under conditions of controlled CO partial pressures. Turn-over-frequencies are evaluated as a function of the film composition and stoichiometry. Aberration-corrected Z-contrast (HAADF) scanning transmission electron microscopy is an invaluable tool for examining the structure of catalysts. Imaging of individual columns from a glancing-angle deposited film reveals gold incorporation as both isolated atoms and as nano-clusters in the anatase. For dense films prepared by symmetric co-deposition, gold aggregates as thin disk-shaped particles or sub-nanometer clusters. Acknowledgement: This work was supported by the US DOE Division of Materials Science under contract DE-AC05-00OR22725 managed by UT-Battelle, LLC.

9:30 AM O1.5
Hierarchical growth and high-yield synthesis of 1D polar surfaced dominated ZnO nanostructures. Pavlin Gao and Zhong Li, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Structurally, semiconductor and piezoelectric zinc oxide has two important structure characteristics: the multiple and switchable growth directions: <0110>, <2110>, and <0001>; and the [0001] polar surfaces. Syntheses of novel 1D ZnO nanostructures and the fundamental physical and chemical understanding of these processes is the key to integrating nanomaterials and nanodevice application. A combination of these distinct growth characteristics results in a group of unique and novel polar surface dominated nanostructures, including nanocantilevers [2], nanosprings [3], nanopropellers [4] and nanorarchitecture [5] such as various types of nanorings, nanobows, platelet circular structures, etc.. The growth mechanism is proposed to be the self-balancing between tunnel electron transport and electrostatic energy induced by +(-0001) polar surfaces and polar surface induced...
asymmetric growth [2, 6]. Based on an improving understanding and by controlling the growth kinetics through refining parameters such as temperature and duration of the sol-gel processing, high pressure, low-temperature process, the nanoscale noble metals have been successfully synthesized at high yield (> 50%) [7]. Our experiments indicate that doping is not necessary for forming the colloidal nanoparticles, and the nanoscale noble metals, and the pre-growth low pressure seems to be the key. The nanobelts that form the nanoscale noble metals grow along [1-10], and the ones that form the nanowires/nanowires grow along [10-10]. It is suggested that planar defects play an important role in the growth of the noble metals. This work makes it possible to synthesize high purity, high yield, and high aspect ratio nanowires, opening the door for systematically understanding the properties and applications of semiconductor and piezoelectric nanoscale devices. [1] "Single-crystal nanowires formed by epitaxial self-cooling of polar-nanobelts", X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science, 303 (2004) 1348. 2) "Induced growth of asymmetric nanotube arrays on polar surfaces", Z.L. Wang, X.Y. Kong and J.M. Zhang, Phys. Rev. Lett. 91 (2003) 185502. 3) "Spontaneous polarization-induced nanobelts, nanowires, and nanonanofibers of piezoelectric nanobelts", X.Y. Kong and Z.L. Wang, Nano Letters, 3 (2003) 1625. 4) "Nanopropeller Arrays of Zinc Oxide", P. X. Gao and Z. L. Wang, Appl. Phys. Letts., 84 (2004) 2883. 5) "Nanorattles of semiconducting and piezoelectric zinc oxide", P. X. Gao and Z. L. Wang, J. Appl. Phys., 97 (2005) 044304. 6) "Substrate atom-termination induced anisotropic growth of ZnO nanowires/nanorods by VLS process", P. X. Gao and Z. L. Wang, J. Phys. Chem. B, 108 (2004) 7534. 7) "High-yield synthesis of single crystal nanoscale of ZnO", P. X. Gao and Z. L. Wang, Small, 2005, in press. 8) Research is supported by NASA, NSF and DARPA. 9) Details can be found at: www.materia.gatech.edu/zlwang. *email: zhong.wang@mse.gatech.edu


The understanding of the surface properties of gold-based alloy nanoparticles is essential for exploiting their unique catalytic properties. This study reports findings from an FTIR investigation of CO adsorption on the surface of silica-supported gold-platinum nanoparticles. Gold-platinum nanoparticles of 2-5 nm sizes with controlled bimetallic alloy compositions were studied as a model system. The nanoparticles were characterized by TEM on silica supporting materials, and calculated at controlled conditions. By comparing the spectroscopic characteristics with those of the monometallic nanoparticle counterparts, the CO stretching bands for the adsorption on the bimetallic nanoparticle catalysts are found to fall distinctly in between those for the monometallic Au and Pt nanoparticle catalysts. The finding is significant because it has substantiated the surface alloy character of the bimetallic nanoparticle catalysts. New insights into the correlation between the bimetallic composition and the surface binding properties, along with their implications to the design of gold-based bimetallic nanoparticle catalysts, are discussed.

10:30 AM Q17 Selective Oxidation using Supported Nanocrystalline Gold. Graham John Hutchings, Chemistry, Cardiff University, Cardiff, Wales, United Kingdom.

There is currently great interest in the use of supported gold nanoparticles as catalysts for a range of chemical reactions. In this presentation the use of gold catalysts for selective oxidation will be explored. In particular two applications will be described: (a) the preferential oxidation of CO in the presence of excess hydrogen, carbon dioxide and water for use in the clean up of hydrode for fuel cells, and (b) the direct oxidation of hydrogen with oxygen to form hydrogen peroxide using the preparation and characterization of selective gold catalysts for these applications will be described. The preparation method is found to be critical for the preparation of stable catalysts. In both cases in the way in which the catalysts are calcined is found to be the major factor controlling their catalytic performance.

11:00 AM Q18 Steam Reforming of Propane over Nanostructured Complex Oxide Catalysts. Matthew Bell and Jacob Y. Yang; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Two new classes of catalysts, barium hexaaluminate (BHA) supported catalysts and nickel alumina, were developed for steam reforming to generate hydrogen for fuel cell applications. BHA nanoparticles of excellent thermal stability and high surface areas were produced by reverse microemulsion sol-gel processing, and doped or doped with nickel. Nanocrystalline nickel aluminae at different Ni/Al ratios were prepared by chemical co-precipitation. For the steam reforming of propane, excellent catalytic activity and hydrogen selectivity were achieved with the BHA-supported catalysts and nickel-impregnated BHA with highly dispersed nickel. For the nickel aluminate system, nanocrystalline catalysts with high Ni/Al ratios provided greater activity than those with low Ni/Al ratios. These two classes of catalysts were further compared with vapor-grown nickel metals to achieve improved catalytic activity at low temperatures. The optimized systems were examined as a function of reaction temperatures and feed compositions.

11:15 AM Q19 Active site Identification for Vinyl acrylate Synthesis on Pd-based Catalysts. Dheeraj Kumar, Minglu Shen, Cheol Woo Yi, Vihan Han, Kai Luo and David Wayne Goodman; Chemistry, Texas A&M University, College Station, Texas.

Vinyl acrylate (VA) is a very important precursor used in the synthesis of many polymeric products and is industrially produced by acetoxylation of ethylene over Pd-Au catalysts with high selectivity. Although this reaction has received considerable attention, no consensus exists with respect to the reaction mechanism. In the present study, a combination of surface science techniques and kinetic measurements has been used to address the details of this important reaction. On supported and unsupported Pd and Pd-Au catalysts the reaction rates were found to be: Pd(100) < 5 wt% Pd/Pt(100) < Pd(100) < 5 wT% Pd/SiO2(100) < < 1 wt% Pd/SiO2(100). Moreover, the addition of Au to Pd/SiO2 catalysts significantly enhances the VA formation rate and selectivity. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd(100) and Pd(100) was found to be the Curta no catalysts obtained from the hydrothermal treatment of titania nanotube suspensions under an acidic environment resulted in the formation of single-crystalline anatase nanoparticles with a specific-cristobalite growth direction. The crystal size of the anatase nanoparticles obtained from the hydrothermal treatment increased with the pH of the suspension, and nanorods with an aspect ratio up to 6 and a long axis along the nanowire [001] were observed at a pH slightly less than 7. A mechanism for the nanorod-to-rod transformation has been proposed in terms of the crystalline structures of the tubes and rods. The local shrinkage of the tube walls form anastase crystallites and the subsequent oriented attachment of the crystallites have been suggested to be the key steps involved in the nanorod formation. As to the application of catalysis, a process was developed to prepare high activity catalysts by loading active metal oxides on large surface area TiO2. Cu-intercalated nanotubes can be obtained by adding Cu(NO3)2 during the hydrothermal NaOH treatment on TiO2. Upon calcination the nanotubes transformed to large surface area TiO2 aggregates containing highly dispersed Cu. The Cu-planted TiO2 was shown to have high activity in selective catalytic reduction of NO with NH3.

11:45 AM Q11 Nanoholes Formed in Silicon by Wet Etching using Metal Particles as Catalyst. Kazuya Tsujino and Michio Matsunaga; Research Center for Solar Energy Chemistry, Osaka University, Osaka, Japan.

We found that deep cylindrical nanoholes were formed in silicon by chemical etching in a solution containing HF and H2O2 using silver nanoparticles loaded on a silicon surface as catalyst (Adv. Mater., 17, 1045 (2005)). During the etching process, the silver particles gradually sank into silicon in the <100> direction, forming cylindrical nanoholes with diameters ranging from 50 nm to hundreds of microns, which was comparable to those of silver particles. The depth reached 500 μm when the etching continued for 10 h. Here, we report the morphologies of holes produced in the early stage of etching. The influence of H2O2 concentration on the etching is also discussed. P-type Si(100) wafers with a resistivity of 9 - 11 Ωcm were used. Silver particles were deposited on the surface by dipping the wafers into an aqueous solution containing 10−7 M AgNO3 and 10−7 M NaOH for 20 min. The sizes of the particles were mostly between 30 nm and 100 nm. Then,
chemical etching was performed in aqueous solutions containing 4.5 M HF and 0.79 M H2O2 for 1 min. On the top of the surface, a microporous layer of about 10 nm in thickness was observed, and cylindrical holes perpendicular to the sample surface were observed up to 2 μm in depth. An Ag particle was observed at the bottom of each cylindrical hole. This indicates that silver particles sink into silicon and form dendritic branches. However, in the region near the sample surface, the holes horizontal to the sample surface were observed. When the etching was performed in a solution containing 4.5 M HF and 0.16 M H2O2 for 5 min, holes and trenches were observed on the surface. The directions of trenches were perpendicular to each other, indicating that the directions were <100>. The trenches had the widths comparable to the diameters of the holes. Hence the trenches were probably formed by horizontal growth of the holes. In the bulk of silicon, cylindrical holes were generated and particles were observed at the bottoms of holes. The depths of the holes formed in Si reached 3 μm. In this case, the microporous layer was hardly observed on the surface. We consider that the microporous layer is formed on the surface by chemical reactions which are generated in silicon when excess H2O2 is present in solution, and that the nanoholes are produced by other chemical species, such as OH radicals.

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**SESSION O2: Biosensors I**

*Chairs: F. P. Zamborini and Chuan-Jian Zhong*

*Monday Afternoon* - *Presentation 28, 2005*

*Room 200 (Hynes)*

1:30 PM *O2.1*

**Deposition of Rare-Earth Doped Nano-particles on Multi-Wall Carbon Nanotubes for Biomedi cal Diagnosis and Treatment.** Wei Wang¹, Jie Liu², Guokui Liu³, Peng He¹, Lumin Wang⁴, Rodney C. Ewing² and Donghu Shu¹

1 Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 2 Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, Michigan; 3 Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

Surface multi-functionalization of nanotubes or nanoparticles is often required in the fields of biomedical science and nanotechnology. In cancer diagnosis for instance, not only does the nanoparticle need a cavity structure for storage and delivery of drugs, but also be luminescent for detection. Here, we report a novel solution method for the deposition of nano-sized europium doped Y2O3 on the surfaces of multi wall carbon nanotubes (MWCNTs). The surface morphologies and microstructure have been characterized by high resolution transmission electron microscope (HRTEM) and electron diffractions. Fluorescent spectrometer measurements indicated that the surface functionalized MWCNTs exhibit luminescent emission in the visible light range. The deposition of optically-activated rare earth nanoparticles on the surface of carbon nanotube may find an important application for the cancer diagnosis and treatment. The nucleation and growth mechanism of rare-earth doped nano-phosphors on MWCNTs were discussed.

1:45 PM *O2.2*

**'Bricks and Mortar' Assembly of Nanoparticles using Polymers and Proteins.** Vincent Rotello, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts.

Self-assembly is an essential process in biological systems, providing the diverse range of highly ordered structures observed in living organisms. Adaptation of self-assembly processes to the controlled assembly of nanoparticles using polymers and biopolymers provides a useful method for the creation of novel higher-order architectures. These ‘bricks and mortar’ assemblies feature structural and dynamic attributes comparable to those used to provide nanoscale chemical properties. The application of this self-assembly strategy to the creation nanocomposites and biomimetic complexes featuring new catalytic, magnetic and plasmonic properties will be discussed.

2:15 PM *O2.3*

**Site-specific Labeling of Active Proteins with Gold Nanoparticles.** Marie-Eve Aubin¹ and Kimberly Hamad-Schifferli²,³

1 Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2 Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Nanoparticle conjugation to proteins is challenging as there are many residues which the nanoparticle can non-specifically adsorb to. This is problematic as non-specific adsorption can denature the protein, altering structure and thus compromising protein activity. We study site specific labeling of two enzymes, Ribonuclease S and Cytochrome c, with the goal of understanding conditions that minimize non-specific adsorption and optimize structure and activity. Ribonuclease S is a two-piece protein made of S-peptide and S-protein. 3nm gold nanoparticle is attached to a mutated cysteine residue on the S-peptide. The altered enzymatic activity of gold labeled Ribonuclease S is determined using RNA substrate modified with a fluorophore-quencher couple. Cytochrome c is covalently linked to 2nm nanoparticles with negatively charged or neutral ligands through interaction with a surface cysteine residue. The labeled protein is characterized with circular dichroism, UV-visible absorption, and cyclic voltammetry. The electron transfer activity was probed with interaction with Cytochrome c Oxidase. For both proteins, agarose gel electrophoresis was used to determine optimal reaction stoichiometry and to probe non-specific adsorption between the nanoparticle and protein.

3:30 PM *O2.4*

**Chemical and Bio-Sensing Properties of Silicon Nanowires.** Shuит-tong Lee, COSDAF and Department of Physics Science & Materials Science, City University of Hong Kong, Kowloon, Hong Kong SAR, China.

One-dimensional nanostructures are good candidates for ultrasensitive, miniaturized molecular and biological sensors in many applications. Because of the high surface-to-volume ratio of nanostructures, their electrical properties are sensitive to the surface species such that small detection becomes possible. Silicon nanowires (SiNWs) are particularly interesting because their surfaces can be readily functionalized to act as electron-transfer mediators and immobilizing matrices for designing sensors for a wide range of biological or chemical molecules, as well as for chemical and catalysis applications. In this presentation, we report the unusual sensitivity of electrical properties of SiNWs towards gas molecules. In addition, hydrogenated SiNWs are shown to be unusually reactive towards O2; they can reduce metallic ions to metals and hydrocarbons to carbon nanostructures, respectively, under normal ambient conditions. These interesting properties of SiNWs are useful for gas sensing and chemical applications, as well as for ultrasensitive, surface-enhanced Raman-scattering detection. Next, we report the use of SiNWs as both the electron-transfer mediator and immobilization matrix together with cyclic voltammetry (CV) to construct biosensors with high sensitivity and selectivity. The capacity of the SiNWs to catalyze glucose oxidation to glucose was used as a model system for the design of glucose sensors which show superior performance characteristics. SiNWs strands were directly fabricated into sensors to measure bovine serum albumin (BSA) via CV method after treatments with HF, AuCl3, and thioacetic acid, respectively. The sensor shows a wide linear detection range up to 1 μmol L-1, high sensitivity (70±mAM/mmol), and good selectivity. Further, long SiNW yarns were similarly modified with AuCl3 to serve as sensor to detect calf thymus DNA via CV, which shows good sensitivity and a wide linear range up to 500 micromol/mL.

3:45 PM *O2.5*

**Biphasic Polymer Nanocolloids.** Kyungho Roh³, Solsoes Olan0¹, David C. Martin²,³ and Joerg Lahann¹,²,³

1 Chemical Engineering, University of Michigan, Ann Arbor, Michigan; ²Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; ³Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan.

Objects with diameters in the nanometer range have properties that are distinctly different from bulk solid-state materials, including unique magnetic, electronic, optical, chemical, and biological characteristics. This observation has fueled the vision of future bioanalytical devices spawned from tiny functional components. In this concept, the controlled distribution of matter (patchiness) is important for creating anisotropic building blocks that respond with preferential alignment to the application of external fields. As a consequence, the control of materials distributions is a measure of a nano-object's introduction, size, and structure. The size of the micron-manipulated object - beyond size and shape. Although the reliable and efficient fabrication of building blocks with controllable materials distributions will be of interest for many applications in research and technology, this synthesis has been addressed only in a few specialized cases, and suitable fabrication methods with general applicability are still missing. We will report on the design and synthesis of polymer-based particles with two distinct phases. The biphasic geometry of these Janus particles is induced by the simultaneous electrolytodynamic jetting of parallel polymer solutions under the influence of an electrical field. Electrofluid jetting is a process to generate liquid jets by rapidly electrostatic forces. The high electrical potentials (typically several thousand volts) applied between the jetting liquids that are fed through a capillary and a collecting substrate will induce jetting of the charged liquid. The final morphologies of the resulting nanoparticles are mainly determined by the properties of the jetting liquids and the process parameters. In our system, preferential compartmentalization is maintained throughout jetting and solidification and results in biphasic particles with diameters between 200 and 1000 nm. Using transmission electron microscopy, scanning
electron microscopy, and scanning laser confocal microscopy, we demonstrate the applicability of the process to control size, shape, and material properties at the nanoscale level. Thus, a method that provides unimolecular, or reagentless, sensors for small molecules using metalloprotein-attached semiconducting nanoparticles is reported. These findings, validating electron transfer involvement in this process, and the extended applicability of the system using CdSe/ZnS core-shell nanoparticles will be discussed.

4:30 PM O2.7
Sasib Das and Mustafa A. El-Sayed; Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Tech, Atlanta, Georgia.

Experimental observations and theoretical treatments are carried out for the band shape and relative intensity of emission from gold nanorods of various aspect ratios in the range between 2.0 (1.5 theory) and 6.3 (9 theory). The calculation of the fluorescence spectra requires knowledge of the nanorod size distribution, the enhancement factors and the shape of the unenhanced fluorescence spectrum. The comparison between the observed and calculated fluorescence band shapes is found to be good. The calculated changes in the relative intensities with aspect ratios are found to be much greater than that observed experimentally. This is due to the fact that for the observed emission of all the rods studied, nonradiative processes dominate the relaxation mechanism of the excited state, a fact that was not included in the theoretical treatments. Experimental results and theoretical treatments will be presented.

4:45 PM O2.8
Using Metalloprotein-Semiconducting Nanoparticle Hybrids for Regenerable Biosensing of Small Molecules. David E. Benson and Marinella G. Sandros; Chemistry, Wayne State University, Detroit, Michigan.

Development of semiconducting nanoparticles attached to designed metalloproteins for the use in detection of sugars and other small molecules will be described. Such hybrid assemblies are important in developing in vivo fluorescent biological assays for and nanodevice responses to small molecule analytes. As opposed to cell or protein detection by semiconducting nanoparticle biocatalysts, a modular method for small-molecule detection by semiconducting nanoparticle biocatalysts that overcomes these difficulties is reported. This method uses interactions between a protein-attached Ru(II) complex and the surface of a CdSe nanoparticle to alter the CdSe nanoparticle fluorescence emission intensity. As metalloproteins to metalloprotein binding in this proof-of-principle system and the protein conformation changes which changes the Ru(II) complex-CdSe nanoparticle interaction. The specific Ru(II) complex used in this report has a Ru(III/II) reduction potential around 1.40 mV versus SHE that, reportedly, facilitates reduction of the CdSe excited state forming the CdSe anion. CdSe anions have been reported to be non-fluorescent, thus making fluorescence emission intensity a viable method for detecting Ru(II) complex-CdSe nanoparticle interaction and a reporter of metalloproteins binding. Four different surface-cysteine, Ru(II)-attached metalloprotein binding proteins have been used for metalloprotein dependent CdSe emission intensity studies. With 3.0-3.5 nm diameter CdSe nanoparticles, all four ruthenated metalloprotein binding proteins display similar increases in CdSe emission intensity (~ 140%) upon saturated metalloprotein binding and maltose affinities (Ka ~ 1x10^7 M^-1). The only difference between these four systems was the sample-to-sample variation in maltose-dependent response. However, the CdSe nanoparticles can be independently loaded with biomolecules or selectively modified with model ligands, as confirmed by confocal microscopy and transmission electron microscopy. The fact that the spatial distribution of matter can be controlled at such small length scales will provide access to previously unknown anisotropic materials. This novel type of nanocollaid may enable the design of multicomponent carriers with interesting properties for drug delivery, molecular imaging, or guided self-assembly.

SESSION O3: Poster Session: Nanoparticles and Nanostructures in Science and Catalysis

Chairs: F. P. Zamborini and Chuan-Jian Zhong
Monday Evening, November 28, 2005
8:00 PM
Exhibition Hall D (Hynes)

O3.1
Piezoresistivity in Films of Nanocrystalline Manganites. Jayanta Sarkar* and Arup Kumar Raychaudhuri*; 1Physics, Indian Institute of Science, Bangalore, Karnataka, India; 2Physics, S. N. Bose National Centre for Basic Sciences, Kolkata, West Bengal, India.

The perovskite oxides are very susceptible to lattice distortion. The electrical and magnetic properties most depend on the MnO6 octahedra. Any change of the Mn-O-Mn bond angle or length can change its properties. Hydrostatic strain and biaxial strain greatly affects its ferromagnetic transition temperature, Tc. The electrical properties in thin films of CMR oxides are influenced by strain, microstructure and the grain boundaries. All the strain effects that have been reported so far are on the epitaxial films. The change of the electrical properties with strain leads us to check whether these CMR oxides show any piezoresistive effect or not. The investigations on piezoresistivity of manganites have been taken up for two reasons. Firstly, to search for a new material that in principle can be adapted to various surfaces and secondly, a basic physics reason where one expects that manganites can change resistance when a uniaxial pressure is applied on them. This is due to Jaw-Teller distortion around the Mn^3+ ions, which can be tuned by biaxial or uniaxial stress. We have done our study on LSCO, LaMnO3 and LSGM polycrystalline films grown on Silicon. Chemical solution deposition technique was followed for the preparation of the films. Controlled straining of the film on the silicon substrate was performed by a cantilever arrangement. One end of the Si substrate was clamped and other end was pushed by a plunger which makes the cantilever to bend in flexure. A Wheatstone bridge arrangement was made to detect the resistance change. We have seen the gauge factor (G) which is the fractional change in resistance (∆R/R) per unit strain comes out to be ~ 10. The resistance increases on tensile strain and reduces by nearly the same amount on compressive strain.

O3.2
Linearized Quantum Conductivity of Small Clusters Synthesized of Ga or In Atoms with As. Lindnala A. Pothar.
Chemistry, Western Kentucky University, Bowling Green, Kentucky.

Recently [1], the linear response theory formalism was generalized to include strongly spatially inhomogeneous quantum systems (such as small clusters, semiconductor quantum dots, atomic clusters, atoms, molecules, etc.) in external electro-magnetic fields. Explicit linear (with respect to the fields) contributions to the longitudinal and transversal quantum conductivity (LLC and RT, respectively), generalized susceptibility, and dielectric and magnetic susceptibility tensors have been derived in terms of the equilibrium retarded two-time temperature Bogoliubov-Bychkov’s Green functions (BTGFs). The Fourier-images of these functions satisfy an (infinite) system of algebraic equations (due to Zubarev and Tserskovnikov, or ZT), as opposed to an infinite system of integro-differential equations specific to other Green functions-based approaches. The ZT-system of algebraic equations can be solved in a desirable approximation by the generalized continuous fraction method, thus relating the BTGFs to the charge carrier energy spectra. In this study, the above approach is applied to calculate the LLC of several pre-designed artificial clusters of Ga and In atoms with As that can be used as computational templates for building units of sub-nanoscale heterostructures for tunable sensor development. The equilibrium electronic energy spectra of the clusters have been computed by the restricted Hartree-Fock (RHF) - open shell HF (ROHF) and multi configuration self-consistent field (MCSCF) methods using GAMESS software. The RHF-ROHF/MCSCF data so obtained have been utilized in the explicit expressions for the BTGFs of the studied clusters to compute the BTGFs, and the latter have been used in the explicit expression for the LLC of Ref. 1 to calculate the LLC of the studied clusters. While direct comparison of the obtained theoretical results with experimental data is not possible at present due to the absence of experimental data for such small clusters, the theoretical results have

**O9.3 Enhanced Hydrogen Sensing at Room Temperature by Pd-Functionalized ZnO Nanorods. Li-Chia Tien1, Hung-Ta Wang2, Patrick Saldik1, Byoung San Kang3, David Norton1, Fan Ren1 and Stephen Pearton1.1 Materials Science and Engineering, University of Florida, Gainesville, Florida; 2Chemical Engineering, University of Florida, Gainesville, Florida.

The hydrogen sensing property is found to be greatly enhanced by Pd-functionalized ZnO nanorods. The addition of sputtered-deposited Pd clusters to the surface of ZnO nanorods produces a significant increase in sensitivity for hydrogen detection at room temperature. Pd-functionalized ZnO nanorods show a pronounced response after exposure of hydrogen concentrations in N2 of 10-500 ppm by five larger than nanorods without Pd. The detection of hydrogen down to <10 ppm, with a relative response of >2.6% at 10 ppm and >4.2% at 500 ppm H2 in N2 after 10 minutes exposure. There was no response to oxygen or nitrogen at room temperature. The initial conductance recovered within 20 sec by exposing the nanorods to air. Moreover, the sensor operated at 0.5 V and was at a power level of <0.4 mW.

The results show that Pd-functionalized ZnO nanorods could be used for practical applications in hydrogen-selective sensing at ppm levels.

**O9.4 Controlled Synthesis of Ag2Se and Cu2-xSe Nanoparticles from Single Precursor [P3bH3] 3M2(SeC=O)(PbH)2 (M = Ag, Cu). Meng Tack Ng and Jagadese J. Vittal; Chemistry, National University of Singapore, Singapore, Singapore.

Orthorhombic Ag2Se (nanocubes and faceted nanocrystals) and cubic Cu2-xSe (twinned nanocrystals, nanorods and faceted nanocrystals) nanoparticles have been synthesized by thermolysis of the corresponding triphenylamine terminated selenolates [P3bH3] 3M2(SeC=O)(PbH)2 (M = Ag, Cu) in suitable surfactants. The morphology and the size of the synthesized Ag2Se nanoparticles are found to be strongly dependent on the heating duration, temperature and the amount of PbH2 used.

A systematic study of the shapes of Ag2Se nanoparticles indicates that the concentration of nuclei in the reaction solution is responsible for the final morphology of the Ag2Se nanoparticles. Meanwhile, the morphology of the Cu2-xSe nanoparticles is mainly dependent on the nature of the surfactants. These nanoparticles are characterized by X-ray powder diffraction (XRPD) and high resolution transmission electron microscopy (HRTEM).

**O9.5 One-Step Flame Synthesis of Pt/Ba/Al2O3 NO Storage Reduction Catalysts. Bart Szczep1, Marco Piccinini1, Marek Maciejewski1, Balazs Pandor and Sotiris E. Founti2.1 Particle Technology Laboratory, ETH Zurich, Zurich, Switzerland; 2Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland.

Engines operating under lean conditions exhibit higher fuel efficiencies than those nowadays stoichiometric engines. However, in the presence of excess oxygen in the exhaust gas, conventional three-way catalysts are not capable to remove NOx sufficiently. In the NOx storage-reduction (NSR) concept NOx is stored under lean conditions and reduced into N2 during fuel rich periods. Pt/Ba/Al2O3 NSR-catalysts were prepared by a novel two-nozzle flame spray pyrolysis (FSP) process. The materials were characterized by transmission electron microscopy (TEM), CO chemisorption, nitrogen adsorption (BET), X-ray diffraction (XRD), and temperature programmed decomposition (TPD). The behaviour in the storage and reduction of NOx was investigated by a NO-pulse technique. Depending on the catalyst geometry, the use of two separate nozzles, one as aluminium and the other as barium source, resulted in the formation of individual Al2O3 and crystalline BaCO3 nanoparticles, whereas the materials prepared by a single nozzle process showed only amorphous Ba species. The crystalline barium carbonate showed a low thermal stability (decomposition below 900 °C) and no rbublik-like behaviour (decomposition above 900 °C) was observed.

**O9.6 Ability of Cathodoluminescence Measurement for Testing SnO2 Films and Powder Synthesis of Gas Sensing Applications. Gennadii Korotevchenko1, Mikhail Naorov1, Vladimir Brinzari1, Albert Cirera2, Albert Cornet2, Kengo Shimanno2 and Noboru Yanazoe2.1 Lab. of Micro- and Optoelectronics, Technical University of Moldova, Chisinau, Moldova; 2Dept. of Electronics, University of Barcelona, Barcelona, Spain; 3Faculty of Engineering Sciences, Kyushu University, Fukuoka, Japan.

Thin (30-100 nm) nano-sized SnO2 films doped by one of the metals from following rank - Fe, Co, Ni, Cu (0-16 wt %) were deposited by spray pyrolysis. SnO2 powders doped by Pt or Pd (0-10 at %) were synthesized by sol-gel method. Cathodoluminescence (CL) spectra were detected in the range 300-800 nm at room temperature by SEM, XRD, and AFM study shown that in the range of pyrolysis temperatures 400 - 500 °C the incorporation of second phase has weak influence on both the size and the shape of grain crystallites. At the same time it was found that cathodoluminescence spectra are very sensitive to the film nanostructure, type and amount of additives. Moreover, they demonstrate different shapes and nonmonotonic modification due to the change of doping level. The introducing already low concentration of dopants (~1% at 5%) dramatically changes the shape and intensity of cathodoluminescence spectra as compared with undoped SnO2. Considerable concentration of additives, apart from additives of Co, reduces the CL intensity in all spectral range of measurement. As a rule nanostructured SnO2 with D > 10 nm had complex CL spectrum. When the grain size increased, the narrowing of half-width of CL spectra to 100 - 150 nm, the increase of CL intensity, and the shift of CL maximum in the long-wave region took place. It was established interesting transformation of CL spectra during doping by Pt and Pd, which confirms the formation of the tails of density states distribution near the top of valence band.

From our opinion the measurement of CL may be used for supplementary characterization of nano-sized oxide films. The attempt of explanation of mentioned above behavior and some details of composite metal oxide formation are discussed.


Much like the wide commercial adoption of the transistor, the light emitting diode (LED), and the semiconductor laser, biosensors will only reach broad applications when issues of performance, manufacturing cost, and ruggedness can be addressed simultaneously. Over the past 15 years, a wide variety of optical devices and phenomena have been adapted to the task of detecting biochemical interactions without the use of labels. Of these methods, only surface plasmon resonance (SPR) has gained commercial acceptance. Due to the high cost/complexity and low throughput of commercial SPR systems, it is used mainly for protein-protein kinetic binding characterization within core facilities of pharmaceutical companies. These assays represent only a small fraction of those performed in life science research. Photonic crystal biosensors solve the problems of sensitivity, cost, and throughput in an elegant manner. They provide extremely narrow resonant behavior, the resonant characteristics are readily tuned by adsorption of biochemical material, they can be manufactured inexpensively, and they can be measured simply by illuminating with white light. Due to these fundamental properties, photonic crystal biosensors will be able to replace many assays that can currently only be performed using fluorescent tags. By reducing assay complexity, photonic crystals will be used widely in the fields of pharmaceutical research, environmental monitoring, and diagnostic testing where biosensors have not been commercially feasible in the past. In this work, a surface structured photonic crystal is produced incorporating a nanoporous glass material. The low refractive index of the nanoporous glass enables a higher sensitivity to be achieved than any previously reported photonic crystal biosensor. Although the device structure requires sub-micron patterning of the nanoglass material, uniform fabrication of this structure over large (3x5-inch) surface areas on inexpensive glass substrates has been achieved without photolithography through the use of an imprinting process. To our knowledge, this is the first report of such an imprinting process used to impart a pattern to a nanoporous glass film. The presentation will describe the sensor design, fabrication process, chemical surface activation, and incorporation of the large area sensors into standard format 96-well microplates. Sensitivity characterization has been performed in which the nanoporous-based biosensor is compared side-by-side with plastic-based photonic crystal biosensors reported previously. The imprinting process has demonstrated excellent repeatability and uniformity, and thus promises to be a useful method for manufacturing this type of sensor at low cost.

**O9.8 Effect of Zinc Oxide Nanocrystals in Mediums Containing E. coli and C. Xerobacter Bacteria. Javier Avalos1, Brian Mercel1, Onayra Rivera1, Stephanie Santos2, Nicole Villalba3, Yahira Baez1, Jose Gaudier1, Oscar Peoral-Perez2, M. S. Tomar2, A. Parra-Palomino2 and Amanil Ruiz-Mendoza2.1 Science and Technology, Metropolitan University, San Juan, Puerto Rico; 2General Engineering-Materials Science and Engineering, University of Puerto Rico, Mayaguez, Puerto Rico.
The present investigation is centered on the study of the growth curves of E. coli and C. xerosis bacteria in presence of nano particles of Zinc Oxide. Previous works demonstrated the sensibility of the bacteria, when these were reproduced in mediums that contain nanoparticles of luminescent silicon and Cobalt Ferrite. Doped ZnO nanocrystals were obtained by conventional precipitation in ethanol solutions as reported by Spanhel and Anderson for bare ZnO. In our case, the syntheses were carried out under ambient-temperature conditions. The experimental results to E. coli bacteria in contact with a stable growth of nanoparticles of Zinc Oxide have showed a growth curve without adaptation period, moreover a short and slowly logarithmic stage has been observed, reaching the stationary stage on the fourth hour approximately compared with one in absence of the nanocrystals (Figure 2, lower curve). A change in the period life cycle (metabolism) with particulate was observed, the beginning of the mortality stage was observed, and it was not observed with silicon and ferrite. For the case of the bacterium C. xerosis the curve with particulates showed a slow growth along his standard curve, without observing oscillations as it happened with the nanometer silicon. For this bacterium the beginning of the mortality stage is observed when they have particles. For both bacteria with Zinc Oxide nanoparticles this occurs approximately in the ninth hour of initiate the measurement process. The probable interaction of the electric polarity of the bacteria with the magnetic property of the Zinc Oxide nanoparticles should be involved with the observed phenomena.

### O8.11

**The relation between catalytic activity of CO oxidation and support structure in oxidation catalysts using gold nanoparticles.** Shiho Nagano, Koji Tajiri and Yutaka Tai; AIST, Nagoya, Japan.

It is well known that gold nanoparticles supported on metal oxide show surprisingly high catalytic activity for CO oxidation reaction, and that the activity is strongly affected by the particle size. So preparation of the composite materials with size controlled gold nanoparticles is valuable for the investigation of size effects and improvement of catalytic activities. We previously developed the preparation method for size controlled gold nanoparticles supported on aerogels. In that process, thiol-passivated gold nanoparticles dissolved in toluene were adsorbed in the wet gel by immersion, then the composite wet gel was supercritically dried by carbon dioxide medium. After heat treatment to remove thiol capping, composite aerogels having gold nanoparticle catalysts were obtained and then thiol capping was removed by heat treatment in air at 873K. By using the aerogel prepared from same wet gel used for previous method as the support, it was found that obtained composite showed almost no size change of the nanoparticles and high uniformity of catalytic activity. To investigate the limit of this method etc., we studied the effects of the support material on the CO oxidation activity of composite materials prepared by this method. Titanium-coated silica aerogels and aerogels were used for the support. The effects of skeletal structure, surface condition, and density of the gels on the catalytic activity and on the supported condition of the gold nanoparticles were investigated. Catalytic activity was changed with the supports. Density and pore size of the support had little influence on the activity. Composites from aerogel supports showed almost same activity as those from aerogel supports did. Sintering of the support materials changed the activity. It was considered that surface condition of the supports affected the supported state of the gold nanoparticles. For composites from gel supports with rough and large skeletal structure and relatively small surface area, the activity was considerably decreased. It was found that the activity was caused by the change of the size of gold nanoparticles and by supported condition of the nanoparticles on the surface of gels.

### O8.12

**Self Assembled Silver Nanoparticles on Nanostructured Surfaces for Molecular Detection by Surface Enhanced Raman Scattering:** Surjit Chattpadhayay,1 Hung Chun Lo2,1, Keui Hsien Chen2,1,2,3, Shihs Chen Shih2 and Li Chyong Chen2; 1Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; 2Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; 3Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Surface enhanced Raman spectroscopy (SERS) has evolved as a powerful and sensitive tool for detection and identification of a wide range of adsorbate molecules down to the limit of single molecule detection. In this paper we report the self assembly of silver nanoparticles, with less than 10 nm diameter, on a variety of nanostructured surfaces. The surface energies offered by these templates namely, silicon nanotips (SiNT), aluminum nitride nanotips (AlNNT), nanorods (AuNR) and carbon nanotubes (CNT) to an incident flux of silver atoms culminates in organizing silver nanoparticles at an extremely high density on their surfaces that readily exhibit SERS. These one dimensional nanostructured templates are prepared by conventional plasma or thermal chemical vapor deposition (CVD) techniques. Silver has been deposited on these surfaces via ion beam sputtering technique. These specially prepared substrates containing the nanoparticulates on the one dimensional nanostructured surfaces (SiNT) and naturally occurring surfaces such as Rhodamine 6G, or BPE adsorbed on these substrates show SERS reproducibly. Such small size (10 nm) silver clusters are generally prepared by wet chemical techniques which are not suitable in device processes. However our technique in generating SERS active
substrates are entirely plasma based and compatible to device processes. The large surface area of the nonstructured substrates and the extended area of the nanowires distributed on them enable the substrate to behave as reliable and reproducible SERS active substrates even at very low concentrations of the molecules under study. A range of Raman enhancement factors could be obtained using these substrates in the range of $10^2$ to $10^3$.

**O3.13 Controlling the Shape and Length of Gold Nanorods and Nanocubes: the Growth of Rod Using XAS, Tianrun Xue, 1 Department of Chemistry, National Taiwan University, Taipei, Taiwan; 2 Catalysis Research Center, Hokkaido University, Sapporo, Japan; 3 National Synchrotron Radiation Research Center, Hsinchu, Taiwan.

The synthesis of metal nanoparticles with controlled shape and size is important in the present era of advanced materials, as nearly all properties in the nanometer regime depend on shape and size. We demonstrated a new approach, which could fabricate the gold fusiform nanoparticles and nanorods by controlling the volume of growth solution. The shape evolutions ranging from fusiform nanoparticles to monodispersed rod were obtained, the shape control of gold nanostructures could be achieved. Increasing the addition of growth solution can control the length of nanorods. After five additions of growth solution, the length of rods can be extended to 2 $\mu$m, and nanorods with aspect ratios of up to $\sim 50$ could be obtained. Moreover, the X-ray absorption spectroscopy is applied herein to elucidate the growth mechanism of gold nanorods. The gold ions were directly reduced to gold atoms by ascorbic acid during the reaction, and the gold ions on the surface of gold salt that were introduced into the reaction. The extended X-ray absorption fine structure confirmed the formation of gold nanorods after the seeds were introduced and the environment around Au atoms over the reaction.

**O3.14 Growth of Silica Nanowires Catalysted by Pd Ion Implantation into Si(100), Praveen K. Sekhara1, Dinesh K. Sood2 and Shekhars Bhanasi2; 1School of Electrical & Computer Engineering, RMIT University, Melbourne, Victoria, Australia; 2Department of Electrical Engineering, University of South Florida, Tampa, Florida.

Of the numerous one-dimensional structures, the silica nanowires are a subject of intense research in view of their potential for several unique applications such as: localisation of light, low dimensional waveguides, scanning near field optical microscopy (SNOM), optical interconnects on a futuristic integrated optical microchip, biosensors and optical transmission antennae. The vapour-liquid-solid (VLS) mechanism frequently employed to grow silica nanowires depends on availability of a tiny liquid droplet of a catalyst metal. In this work, we have used ion implantation of Pd ions into silicon (100), through a mask, to form nanodusters of Pd to act as such catalysing seeds. Pd ion implantation was performed with a MEVVA (metal vapour arc evaporation) machine at the lowest possible ion implantation voltage (3 kV) in the implanter to produce a stable ion beam was chosen to maximize surface concentration of implanted Pd species. A metal (Al) mask with 14 equi-spaced circular holes each of 4 mm diameter was used in contact with the Si (100) wafer held at a temperature of 650 °C. The silicon was identical and well separated zones of ion implanted regions. Dose was varied from 5E12 to 3E16 Pd ions/cm². The implanted wafer was then diced to produce 14 identical 20mm x 20 mm samples with the implanted region of 4 mm diam in the centre. An open Quartz tube furnace was used for heating to grow nanowires, using Ar as carrier gas at atmospheric pressure. The temperatures of 910, 1000 and 1100 $^\circ$C were chosen on the basis of Pd-Si phase diagram. After growth, the samples were analysed using scanning electron microscopy, Energy Dispersive Spectroscopy (EDS), X-ray diffraction, Rutherford backscattering spectrometry and TEM. After heating at 1100 $^\circ$C for 60 minutes, the ion implanted region showed a dense growth of interwoven nanowires whereas the unimplanted region was devoid of such nanowires, clearly showing the selective nature of the process. The nanowires grew with diameters ranging from about 15 to 90 nm, with lengths varying up to about 50 $\mu$m corresponding to an aspect ratio of up to 3000. The growth and properties of silica nanowires were studied systematically under carefully chosen conditions of ion dose, growth time, temperature and gas flow to understand the mechanism of formation. The vapour-liquid-solid (VLS) model of nanowires formation was shown to be valid for the process. As the implanted sample is heated in Ar atmosphere, the interdiffusion at the Pd-Si interface produces silicide PdSi nanoclusters which turn to liquid drops as temperature is increased further. When these liquid drops are exposed to the gas phase, the vapor pressure will be maintained across the system due to the evaporation of gas (Ar), the VLS model of nanowire growth comes to play. This ion implantation seeding method holds a great potential for facilitating directed bottom-up growth of nanowires on silicon wafers.

**O3.15 A Computational Study on CO Adsorption onto SnO2 Small Clusters, Maria Marzegna, IMM, Sezione di Bologna, CNR, Bologna, Italy.

The focus of this study is on the adsorption properties of the nanocrystalline material and SnO2 has been chosen as the appropriate example. Nanocrystalline SnO2, in fact, has many practical applications for gas sensors but is virtually absent from the current physico-chemical literature on nanomaterials. The purpose of this study is to gain a deeper understanding of its gas-sensing properties in order to better exploit its gas-sensor applications. Therefore model structures consisting on small SnO2 grains have been considered and the adsorbed system is generated by depositing a CO molecule above a single oxygen atom on the grain surface. The calculations illustrate the structural properties of grains, their binding and adsorption energies and their conductance and are based on semi-empirical Hfucce-Fock and scattering formalisms. It has been found that the molecule is stably bonded to the grain without penetration or intermixing and adsorption is not dissociative. These also properties of adsorption on the surfaces of bulk samples. However the analysis of the adsorbed systems indicates that adsorption implies from the molecule being integrated into the grain structure. Furthermore adsorption depends on the grain shape, on the adsorption site and on the orientation of the molecule. These effects do not exist in the bulk, though the values of the adsorption may be similar in the two cases. In agreement with known properties of structures of finite size, the conductance changes with the grain structure and its dependence on the grain size and shape is the same as the one of the binding and adsorption energies.


Recently there has arisen an interest in evaluating Pt-containing intermetallic compounds as potential electrocatalyst for use in direct fuel cells. For a useful evaluation in real working fuel cell conditions, these intermetallic compounds must be available as nanowhiskers. This work describes how such nanowhiskers can be prepared by chemical reduction of organometallic precursors by sodium napthalide in tetrahydrofuran under argon atmosphere at room temperature. This reaction system can be employed to reproducibly prepare a nanopowder of PtPb3 and other intermetallics of interest, which are characterized by xRD, SEM, STEM, EDS and CBED analyses. This synthesis also shows promise toward the development of generalizable methods for preparing intermetallic compounds as nanowhiskers due to the strong reducing ability of sodium napthalide.


Platinum nanoparticles show promise in various applications that include catalysis, sensors, and optoelectronic and magnetic devices. The focus of this study was transmission electron microscopy (TEM) imaging of nanoparticle dispersions and the potential impact of the nanoparticle synthesis method as well as TEM specimen preparation technique on the size distributions measured. For synthesis of the nanoparticles the utility of bis(methylthio)malononitrile and related polycyclodiazorane derivatives were studied as potential substrates for the synthesis and encapsulation of platinum nanoparticles. The potential for oxidative addition versus dative bonding to the nanoparticle was modeled using the reaction between bis(methylthio)malononitrile and cis-[Ru2(C2H4)Pt(PPh3)2] and monitored using 1H NMR spectroscopy. The relative size distributions of platinum nanoparticles were studied via TEM (conventional and high resolution/coupled with X-ray diffraction (XRD)) and extended x-ray absorbed fine structure (EXAFS). While TEM data yielded a size distribution for each sample, XRD (using Scherrer analysis), and EXAFS (using a homogeneous spherical model) were used to determine a “mean” particle size. Both XRD and the square of the volume and EXAFS by less than the volume, XRD is expected to generally yield a larger mean value than EXAFS. TEM data is expected to yield the highest precision. The impact of TEM specimen preparation and nanowhiskers size is expected to be key factors impacting the determination of particle size...

Q3.22 Fabrication and Characterization of Molybdenum Oxide Nanofibers/ Nanowhiskers by Electrospinning. Guan Wang, Katarzyna Sawicka, Yuan Ji, Xiaorong Huang, Michael Dudley and Pulagina-Irene Gunia; Department of Materials Science and Engineering, Stony Brook University, Stony Brook, New York.

Molybdenum oxide/ Poly (ethylene oxide) composite nanofibers were prepared by sol-gel processing and electrospinning technique. By calcination of the composites in the temperature range of 60°C to 600°C, the nanofibers/nanowhiskers were obtained with diameters of 100-nanometer scale. Morphology of the fibers was characterized by SEM. Components and structures of the final products were confirmed by TEM and grazing incidence XRD. Calculation process was studied using DSC and TG analysis. The results showed that crystallinity of the metal oxide nanofibers depended on the calcination temperature.

Q3.23 Synthesis of 2D and 3D Metal Nanoarrays and Semiconductor Nanoparticles in Supercritical Fluid Carbon Dioxide. Carlos Alberto Fernandes, DeLyle Eastwood and Chien M. Wai; Chemistry, University of Idaho, Moscow, Idaho.

Metal and semiconductor nanoparticles of controllable size can be synthesized using microemulsions as templates in different solvents. Two types of microemulsions have been studied using bis(2-ethylhexyl)sulfosuccinate (AOT) and a fluorinated AOT as surfactants for making water-in-oil and water-in-CO2 microemulsions, respectively. Chemical reduction of metal ions (e.g., Au3+) dissolved in the water core of a microemulsion leads to the formation of metal nanoparticles (e.g., Au) with size controllable by the dimension of the water core and the solvent surrounding the microemulsion. By mixing two microemulsions, one containing Cds+ and the other containing S2-, Cds nanoparticles of different sizes can be synthesized using the microemulsion-template method. Binary Cds/ZnS nanoparticles can also be synthesized using this method. Because the solvation strength of supercritical fluid CO2 is tunable by varying temperature and pressure, we are developing techniques for synthesizing metal and semiconductor nanoparticles of controllable sizes using water-in-CO2 microemulsions as templates. The synthesized nanoparticles can be stabilized using an alkanethiol compound. Self-assembly of thiol-stabilized gold nanoparticles has been shown to result in ordered 2D and 3D arrays with sizes in micrometer dimensions. Characterization of these nanoparticles and nanoarrays including luminescence, TEM, SEM, XPS, and XRD are currently in progress and will be published.


Controlling the organization of nanometer scale materials within discrete 1D nanostructures poses an intriguing synthetic challenge. Frequently, obstacles such as solvent phase separation limits controllable precipitation, and/or premature component reactivity limit the fidelity of experimental success. For carbon nanotubes, numerous approaches of encapsulating metallic and semiconductor inorganic materials within the tube interior have been tried with generally mixed success. Often, the means of incorporation rely upon physical based

O3.18 Nano-Plasmonic Building Blocks for Robust Nanoscale Devices. Sudharsan Kumar Padig1, Jorge Quijano1 and Shalini Prasad1,2; 1Electrical and Computer Engineering, Portland State University, Portland, Oregon; 2Bio-medical Engineering, Oregon Graduate institute, Hillsboro, Oregon.

A platform based technique for amplifying signals from micro and nanoscale devices used for monitoring applications has been developed. It comprises of dielectric substrate (SiO2) coated with metallic nanostructures. This results in the generation of Surface Plasmonic Waves (SPW) that in turn results in signal amplification. With increased interest in achieving better signal-to-noise ratio from miniaturized devices, there is a tremendous need for achieve reliable signal amplification. The output voltages associated with these devices are in the order of a few tens of mV. In this case, the output voltages are dominated by the noise levels, lowering the signal-to-noise ratio (S/N). This prevents the signals from being analyzed for valuable data. On the other hand, if the acquired signals are processed by discrete components, there is a chance of amplifying the noise levels along with signal level. We overcome this problem through surface plasmonics (SP). The principle of operation is such that, when a light source is coupled to an interface of a metallic nano-structure and a dielectric, Surface Plasmonic Waves (SPW) are generated. The SP waves amplify the electrical field component of the input light wave between 102-104 times. This leads to enhanced output voltages allowing to better amplify, make the signals suitable for data analysis. Hence this technology has potential applications in building robust sub-micro size, ultra-sensitive sensors.

O3.19 Abstract Withdrawn


Sensing devices incorporating monolayer-capped metal nanoparticles have been shown to offer significant benefits in both selectivity and sensitivity when they are used for the determination of volatile organic compounds. Such sensing properties exploit the core-shell structural attributes. While previous work has focused largely on the manipulation of organic shell properties, we are working toward the integration of core-shell nanoparticles, hardware design, and custom software for sensor applications. In this presentation, we describe the fabrication processes for size control of nanoparticles, the derivatization of these cores with capturing ligands, the assembly of the nanoparticles with electronics, the construction of micro-electrode arrays, and the design and optimization of circuit board hardware for organic vapor sensing measurements. The synthesis and the structural properties of the chemically-engineered nanoparticle thin films will be discussed in light of results from TEM, UV-Visible, FTIR, AFM, and sensor testing characterizations. These results demonstrate that the combination of the selective core sizes, ligand shell functionality, electronic hardware, and signal-processing software can be lead to improved sensing capabilities.

O3.21 Products of Thermal Decay of Carbonyl Chalcogenide Metal Clusters as Catalysts for Synthesis of Bamboo-like Nanofibers. Oleg N. Efinov1, Alexei A. Volodin1, Pavel V. Fursikov1, Boris P. Tarasov1, Yurii M Shulga1, Igor I. Khodas2 and Yusif A. Kasumov1; 1Institute of Problems of Chemical Physics, Chernogolovka, Russian Federation; 2Institute of Problems of Microelectronics and High-Purity Materials, Chernogolovka, Russian Federation.

Supported 3d-metal catalysts are widely used to obtain carbon nanotubes and nanofibers by pyrolysis of hydrocarbon gases [1]. To synthesize well-structured nanotubes located on a flat surface metal catalysts representing supported nano-sized metal particles or photochromic thin metal films [2] are effective. Mo-additives to the metals are known to enhance the catalytic performance of such catalysts [3]. One of the main problems of the pyrolytic synthesis of carbon nanotubes and nanofibers is to obtain these products having desired structure with high selectivity. Here we employ a Si/TiNx distribution, and so, this became a focal point of the study. The TEM data collected revealed distributions that were compared with the results of XPS experiments showing XPS data of XRD and EXAFS for providing estimates of particle size were evaluated while the potential impact of nanoparticle synthesis method and TEM specimen preparation technique on TEM data collection was determined.
methods such as capillary force or gas diffusion to introduce the binary or ternary material. Here we report a liquid diffusion, template-based approach to the generalization of semiconductor nanostructures consisting of a rolled tube of the semiconductor TiO$_2$ encapsulating a nanowire of Ag metal within its central core. Previously, we have shown that the undercoordinated character of Ti atoms at the surface leads to enhanced surface reactivity. This unique characteristic is used in transferring the semiconductor template from an aqueous environment to a non-polar solvent for the synthesis of the silver nanowire. We find that the addition of the small ammoniphilic molecule (L-ascorbic acid 6-palmitate) to the surface of the TiO$_2$ tubes is sufficient to act as this phase transfer agent. Upon binding of the ammoniphilic molecule to TiO$_2$, dispersion of the inorganic/organic hybrid from water into hexane is possible. The process occurs, with TiO$_2$ within the interior (hydrophilic) region of the TiO$_2$. To this, we use mixed phase agitator to deliver silver ions to the central core of the nanotube. After penetration of ions into the hydrophobic core, light is used to induce the redox reaction of the ions into nanowires confined to the interior core of the TiO$_2$ tube. We envision this hybrid binary composite consisting of semiconductor wrapped metal nanowire as a building block with potential applications in photo-electrochemical devices, biosensing, and photocatalysis. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under contract W-31-109-Eng-38.

O3.25
Preserved enzymatic activity of glucose oxidase immobilized on an unmodified electrode. Geng Wang and Shi-Yun Yang.
Physics, Hunter College of City University of New York, New York, New York.

Glucose oxidase (GOx) was immobilized on unmodified electrode plane of highly oriented pyrolytic graphite (HOPG) and on the native oxide of heavily doped n-type silicon. The GOx-immobilized electrodes displays the redox behavior of GOx in cyclic voltammograms, indicating direct faradaic electron transfer between the immobilized enzyme and the bare electrode. The measured formal potential agrees with that of the native enzyme, suggesting that the immobilized GOx retained its enzymatic activity. We attribute the observed redox reaction to the electrostatic interaction between GOx and the bare electrode. The functional C-O groups on the edge plane of HOPG and the ultrathin native oxide of silicon provide electrostatic interaction for GOx. The GOx-immobilized electrodes show the correct electrochemical behavior in the presence of glucose, which indicates the catalysis of glucose. Therefore, the response of the electrodes to glucose confirms that the immobilized GOx retained its enzymatic activity. The electrodes show a high glucose detection sensitivity of 22.76 mAMM and a detection limit of 50 nM.

O3.26
University of California, Irvine, Irvine, California.

Micro- or nano-fabrication offers us numerous active devices by patterning small structures on a variety of substrates to meet at least part of our demands in nanotechnology. Since nanotechnology is highly multidisciplinary fields that require contributions from physicists, chemists, biologists, engineers, and materials science, we introduce here a novel 'micro- or nano-fabrications' of functional materials with specific molecular recognitions for bio-sensors and chemical detective technologies as an example of technological emergency. Microcapillary molding (mTM) technique was employed to fabricate micro-patterns and structures based on molecularly imprinted polymer (MIP) system to achieve the functional patterns. Microfluidic synthesis of nano-sized CdS nano-particles is also presented here by fabricating microfluidic reactors, which were designed for micro-synthesis. It utilizes a novel approach for droplet coalesced addition of reactants and their rapid and efficient mixing in picoliter volumes. Following reagent droplet formation, the microfluid channel design results in exclusive fusion of alternate droplets with concomitant rapid mixing of their contents to produce a novel tube-in-tube solution of CdS and S2-ions. The spectroscopic properties of the CdS nanoparticles produced by this method are compared with CdS prepared by bulk mixing.

O3.27
Response of the Luminescence of ZnSe Nanowires to Ambient Gases at Various Pressures. S. K. Hark and C. M. Ng.
Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

ZnSe nanowires were grown by metalorganic chemical vapor deposition (MOCVD) on Si and GaAs substrates. The morphology and structure of the nanowires were examined by electron microscopy and X-ray diffraction. These nanowires consist of tens of nanometers in diameter and are single crystalline in structure [1, 2]. The MOCVD grown nanowires typically show stronger near band edge (NBE) luminescence than those other methods which impinge their large surface to volume ratio. The NBE luminescence was further enhanced by etching away the post-growth surface oxide layer and passivating the surface states of the nanowires in an ammonia sulfide solution. Under the illumination of 325 nm excitation light, the intensity and response time of the NBE luminescence of the passivated nanowires were found to depend sensitively on the type and pressure of gas to which they were exposed [3]. Exposure to H$_2$ and N$_2$ resulted in strong enhancement, but exposure to O$_2$, CO, and air in weaker luminescence. Exposure to inert gases, such as Ar and N$_2$, also induced a change in the NBE luminescence. We have studied the excitation power and pressure dependence of the change and the response time of the NBE luminescence in these gases systematically. To understand these results, we propose a model in which photo-induced adsorption and desorption of gas molecules on the surface of the nanowires are responsible for the change in the radiative recombination rate and result in the observed NBE luminescence intensity. The model is supported by the observations that below band gap excitation of the nanowires does not induce a response when the nanowires are exposed to the gases, and that the response is reversible. The results show that the nanowires may have potential applications as gas sensors. Reference: [1] X.T. Zhang, Z. Liu, Y.P. Leung, Quan Li and S.K. Hark, Appl. Phys. Lett. 83, 5533 (2003) [2] X.T. Zhang, Z. Liu, Y.P. Leung, Quan Li and S.K. Hark, Appl. Phys. Lett. 84, 2641, 2004 [3] K-M. Ip, Z. Liu, C.M. Ng and S.K. Hark, Nanotechnology 16, 1144 (2005) Acknowledgement: The work described in this abstract was partly supported by a grant from the Research Grant Council of the Hong Kong Special Administrative Region, China (Project No. 401033) and a CBUH direct grant (Project code 2060277).

O3.28
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Outstanding physical and chemical properties of ceria nanoparticles such as oxygen storage capacity and high surface area have drawn great attention in catalysis for automobile exhaust treatment and shallow trench isolation chemical mechanical polishing in semiconductor processes. For example, oxygen atoms in fluorite structure of ceria can be released by appropriate treatment and they can provide oxidizing CO and HC, and reduce NOx when it is used as automotive catalysts. Consequently, a number of synthesis methods have been developed to obtain a large amount of uniform ceria nanoparticles. However, physical and chemical properties of ceria nanoparticles are strongly dependent upon the method of synthesis because the environment and conditions of synthesis are different. Therefore, understanding of the characteristics of ceria nanoparticles according to the synthetic route is very useful in selecting a method of synthesis best for a specific application. In this context, we prepared ceria nanoparticles by three different methods: namely, heat treatment, hydrothermal synthesis and solid-state reaction, and investigated morphology, crystal structure, and the oxidation of the synthesized ceria. Morphology was observed by a scanning electron microscope and a transmission electron microscope and the size of crystallite was estimated by Scherrer equations in combination with X-ray diffraction data. Finally, the lattice parameters of ceria nanoparticles were measured by a neutron diffraction method.

O3.29
Deposition of V$_2$O$_5$/TiO$_2$ on ceramic foams for phthalic anhydride catalysis. Heiko Schulz, Bjorn Schimmoeller, Sotiris E. Pratsinis, Anika Baleiss, Andreas Reitzmann and Bettina Kraussaar-Czarnetzki.
1Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland; 2Department for Chemical and Process Engineering, University of Karlsruhe, Karlsruhe, Germany.

The partial oxidation of α-xylene to phthalic anhydride is a highly exothermic reaction. The evolving heat has to be transferred effectively out of the catalytic bed, because hot spots deactivate the catalyst irreversibly and lead to an increased risk of thermal reactor runaway. Ceramic foams of Al$_2$O$_3$ can improve heat transfer compared packed beds of spheres. The open-pore structure and the high void fraction lead to a lower pressure drop over the foam height compared to packed beds. The possible formation of a turbulent gas flow can increase the heat and mass transfer compared to a laminar gas flow in honeycombs. In addition, thermal conductivity and surface properties can be modified by a large variety of foam materials. Thus, it can be expected that foams can combine properties of packed beds and honeycombs in a beneficial way. In commonly used
vanadia/titania catalysts, anatase as titania crystal structure showed higher catalyst activity than other crystal structures. A high dispersion of vanadia on titania is critical for high activity; selectivity is mainly influenced by the chemical characteristics of vanadia itself. Flame synthesis has recently been used for the production of vanadia/titania mixed oxide nanoparticles, containing large anatase fractions. The vanadia content has been varied from 0 - 10 wt.% and the materials exhibited a high vanadia dispersion on titania nanoparticles. No evidence for interstitial vanadia/titania solutions have been found. Production rates ranged from 4 - 200 g/h and specific surface areas from 25 - 190 m²/g. Flame-made particles exhibit, beside the high specific surface area, an open- pore structure that might facilitate mass transfer limited reactions compared to wet-phase made catalysts. The deposition of nanoparticles on foam support led to a different agglomerate and pore size structure than obtained by common multi-step coating techniques in the wet-phase. The open-pore structure was retained, promoting the gas penetration into the active layer. Powders were characterized by various techniques including X-ray diffraction, temperature programmed reduction and Raman spectroscopy and electron microscopy. Powder properties of flame-made and wet-made powders were compared. The influence of key production parameters was investigated. Flame-made powders deposited on ceramic foams exhibited enhanced catalytic activity with comparable selectivity at high conversions compared to wet-phase made catalysts.


CdS films were grown onto glass and InP substrates by chemical bath deposition technique. Resulting optical and electrical properties of the layers as a function of deposition parameters and air annealing are reported. The morphology of the layers can be influenced by adding Cu and Pb salts into the bath used for the deposition. Grain size was reduced in Cu⁺⁺ added layers. Addition of Pb⁺⁺ resulted layer growth of CdPbS. Substrate effect was investigated by deposition of CdS on 100 oriented InP wafer and glass. Epitaxial growth of CdS on InP at room temperature was reported by other authors, but we found In₃S₅ epilayer at the InP/CdS interface. Photoconductivity increases and carrier life time decreases as a result of Cu addition into a bath, or post annealing of CdS layers in CuCl₂ solution. Air annealing at 200°C increases the conductivity of undoped CdS layers, and contrary reduces the conductivity of Cu doped layers. A red shift of spectral sensitivity was observed as a result of Pb salt addition to the deposition bath.

O3.31 Synthesis and Optical Properties of Oriented Cu Nanoparticles. Om Parkash Siwach and P. Sen; Jawaharlal Nehru University, New Delhi, Delhi, India.


O3.32 Surface-Tailored CdSe Quantum Dots/Polymer Composite Films for the Selective and Sensitive Detection of Hydrocarbons. Zheqin Zhao1, Oxnna V. Vassilova2,1, Marina A. Petrakina2 and Michael A. Carpenter1; 1College of Nanoscale Science and Engineering, University at Albany, 2P. and State University of New York, Albany, New York; 2Department of Chemistry, University at Albany, State University of New York, Albany, New York. CdSe quantum dots (QDs) capped with triphenylphosphine oxide (TOPO) as well as a combination of sensing (aromatic-based carboxylic acids and amines) and stabilizing (stearic acid) surface ligands were designed and synthesized in solution phase followed by incorporation into a polymer matrix for subsequent hydrogen detection. The QD-polymer nanocomposite films exhibited a moderate stability against photooxidation even under air, allowing for stable sensing characteristics over a one-week time period. Selection of fluorescent and photoactive QDs in a mixed excited state, with doped polymer sensitizers and the interaction between the QDs and the targeted HC molecules, resulting in a 15pm sensitivity towards xylene in air, is about 3 times the 50nm sensitivity measured in air. Development of new DNA exposure testing procedure a reversible enhancement or quenching of the QD fluorescence was observed. The degree of enhancement or quenching is a function of HC exposure levels, with the quenching process becoming dominant at high carbon concentrations. Details concerning the fluorescence enhancement to quenching inversion point and their respective signal magnitudes displays a dependence on the embedded QD concentration, the type of polymer matrix and the specific HC chemistry. Oxides possessing the perovskite-type structure (ABO₃), with cobalt in the B-site, exhibit outstanding transport properties and chemical activity, which makes these materials suitable for environmental control. These properties can be improved when the oxides are nanostructured and nanoporous, due to their high specific surface areas. One of the goals in this work, was the preparation of nanostructured single-phase powders of GdCoO₃ and members of the solid solutions Gd₀.₇ₓBa₀.₃ₓCoO₃ (x = 0.5, 0.7, 0.9) by a solid reaction method, and testing these materials as possible environmental gas sensor materials. In the preparation of these oxides, the starting aqueous mixtures were made by dissolving stoichiometric amounts of gadolinium, barium, strontium and cobalt nitrates in deionized water, with 0.1 mol of citric acid. X-ray powder diffraction patterns of calcined samples showed that single-phase powders were obtained at 850°C, in air. High-resolution SEM images revealed that nanostructured materials produced for barium and strontium-doped oxides, after a controlled annealing process; whereas micron-sized powders were produced for GdCoO₃. To test these materials as environmental gas sensors, electrical measurements were made on sintered thick films of GdCoO₃, Gd₀.₇ₓBa₀.₃ₓCoO₃ and Gd₀.₇ₓSr₀.₃ₓCoO₃ in air and CO₂. These experiments were performed in a tube furnace under atmospheric pressure and controlled temperature, using the two-point method, with silver wires fixed to the films; the temperature range used was from 100°C to 700°C. The results showed that GdCoO₃ reached its maximum sensitivity to CO₂ at 420°C, whereas for barium and strontium-doped oxides was at 457°C and 444°C respectively. Dynamic response of resistance measurements, performed at a constant temperature of 300°C, revealed that nanostructured Gd₀.₇ₓSr₀.₃ₓCoO₃ and Gd₀.₇ₓBa₀.₃ₓCoO₃ have good selectivity to this gas, whereas micron-sized GdCoO₃ did not show noticeable selectivity.


The optical properties of metal nanoparticle assemblies are a function of the individual particle resonances and interparticle coupling. Here we consider finite assemblies, in particular a DNA-linked core-shell system composed of small metal nanoparticles. These core-shell systems can be designed to exhibit useful optical properties. Here, we describe the properties of a system designed to display a large scattering enhancement upon addition of DNA complement. Core-satellite structures are created in solution from 13 nm and 50 nm gold particles functionalized with S- or S-mercapto-modified oligonucleotides and single strands of DNA. The core particle, by design, is large enough to scatter a detectable amount of light, but small enough so that assembly of a compact shell of 13 nm nanoparticles increases scattering significantly. The system has been characterized by scattering spectroscopy, extinction spectroscopy, and transmission electron microscopy. Scattering at the
plasmon resonance is found to increase dramatically when presentation of complement leads to formation of compact core-satellite structures. The salt and temperature dependence of system assembly is discussed. Tailored nanosystems that self-report via macroscopically observable signals upon the state of assembly or the presence of an analyte have the potential to be useful for real-time monitoring of self-assembly or nanostructure based molecular detection.

Q3.35 Cationic Lipid Modulates Phospholipid Adsorption on Silica.
Sergio P. Moura and Ana M. Carmona-Ribeiro; Departamento de Bioquimica, Instituto de Quimica da USP, Sao Paulo, Sao Paulo, Brazil.

Optimization of bilayer deposition on particles in order to produce biomimetic particles involves control of pH, ionic strength, lipid nature and bilayer physical state, etc [1-4]. Here the effect of molar proportion (M) of cationic and a neutral lipid on bilayer deposition on silica was determined. Dioctadecyldimethylammonium bromide (DODAB) and dipalmitoylphosphatidylcholine (DPPC) over a range of M (0-100 %) were used to prepare vesicles in 1 mM NaCl at the pH of water by ethanolic injection followed by dialysis to eliminate ethanol. Composited vesicles interacted with Aerosil-OX50 and the effect of M on DPPC adsorption, surface potential on particles, particle sizes and colloid stability was determined from adsorption isotherms, dynamic light-scattering, zeta-potential analysis and silica sedimentation imaging from photographs, respectively. For 0-2 % DODAB, adsorption was well above the amount expected for bilayer deposition whereas for 10-20 % DODAB, adsorption was well below this amount. Furthermore, from M = 0, it was possible to modulate DPPC adsorption aiming at bilayer deposition. All data consistently pointed to improved colloid stability upon silica coverage with DODAB/DPPC bilayer. 1.Rapaudo, R.; Carmona-Ribeiro, A.M. J. Colloid and Interface Science, 2005, 284, 292-299. 2. Moura, S.P.; Carmona-Ribeiro, A.M. Langmuir 2003, 19, 6604. 3. Moura, S.P.; Carmona-Ribeiro, A.M. Langmuir 2005, in press. 4. Moura, S.P.; Carmona-Ribeiro, A.M. Cell Biochemistry and Biophysics 2003, in press Financial Support: FAPESP and CNPq.

Q3.36 Nanostructures in Freely Suspended Nanomembranes.
Chaoyang Jiang and Vladimir V. Tsukruk; Materials Science and Engineering, Iowa State University, Ames, Iowa.

Freely suspended nanoscale composite membranes are of interest in the development of microsensors and actuators with potential applications such as micromotors, microfluidic switches, and thermal and acoustic sensors. In this presentation, we will show an easy, low-cost, and efficient method to organize various nanostructures, such as gold nanoparticle and carbon nanotubes, in the freely suspended multilayer membranes that total thickness less than 100 nm. With the combination of spin-assisted layer-by-layer (SA-LbL) assembly, micro-contact printing technique, and sacrificial layer method, the nanoscale objectives can be assembled in the micro-pattern that sandwiched inside the multilayer polyelectrolyte matrix. The morphologies of these membranes were investigated with atomic force microscopy and scanning electron microscopy. From the bulging test, some of these nanomembranes were obtained and compared to that of non-patterned membranes. Moreover, optical properties, such as Surface-enhanced Raman scattering on gold nanoparticle surface and resonance Raman scattering of carbon nanotubes were studies and will be discussed.

Q3.37 Texture formation and optical response in thin liquid crystal film on patterned surface. Dae-Kyun Hwang and Alejandro D. Rey; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

Biosensors based on liquid crystal vision provide an alternative label-free method to detect biological binding events and to use in bimolecular assays on functionalized nano-structured surfaces. In this biosensor, recognition of binding events and quantitative changes in surface biomolecular concentration can be simply observed through changes in optical textures of liquid crystals (LCs) films enclosed in specifically-treated substrates. Determination of these surface-bound biomolecules is made by quantitative interpretation of the optical images of LCs observed between cross-polars using polarized light. In spite of great amount of this biosensor, there is fundamental relationships between optical response and complex LC textures that form the basis of this device, the biosensor function is not fully understood due to multi-dimensional and multi-scale heterogeneities including nano-structured surfaces, molecular size defects in LCs phases, biomolecular size, and micro optical textures. Furthermore, the characterization of surface-induced texture formation and its optical response has not been fully explored. In this paper we study texture formation of LCs in thin LC films placed between patterned surfaces containing a stamped protein region and a non-stamped protein region. The optical response of the textures under cross polarized light using the Finite Difference Time Domain (FDTD) method. The results obtained by the FDTD method are compared with classical matrix-type methods. The two optical methods show significant deviations because the textures of LCs show large multidimensional and multi-scale spatial gradients of the optic axis, which the matrix-type method fails to capture. Based on our computational results, the FDTD method is shown to provide accurate predictions of significant optical features of the textured LC films on the patterned surfaces. The optical computations presented herein indicate that the texture formation modeling may provide a better understanding of biosensors based on liquid crystal vision and eventually leads to an improved functionality and an increased ability to recognize changes in biological interfaces on nano-structured surface.

Q3.38 Biofunctional Probes Built on Carbon Nanotube Scaffolds.

We report the production of a bioactive, functionally gradient coating on a carbon nanotube (CNT) that has been isolated on an inorganic tip that can be integrated into a probe configuration. CNTs offer quasi-one-dimensional structures that can be utilized as biofunctional substrates. The graphene walls of as-produced CNTs are relatively non-reactive with respect to most biological molecules, but through chemical functionalization the CNTs can be made more receptive to biological molecules. The coating is comprised of a mesoporous carbon scaffold under conditions that are conducive to the entrapment of enzymes within the coating. The porosity of the coating can be controlled via colloidal particle size, making the coating versatile in the types of enzymes and molecules that can be immobilized. Bioactivity is confirmed through measurements of the retention of enzyme activity within the coating.

Q3.39 FAD Aerosol Synthesis of Nanostructured Photocatalytic Titania Thin-Films for Hydrogen Production. Rafael McDonald and Pratim Biswas; Environmental Engineering Science, Washington University in St. Louis, St. Louis, Missouri.

The photoplatinization of water using solar energy is a potentially clean and renewable source of hydrogen that is environmentally benign and easily distributed. Light impacting titanium dioxide electodes immersed in water causes the water to split into oxygen and hydrogen. However, pure bulk TiO2 requires uv-light, which is less than 5% of incident solar radiation, for excitation. It has been shown that titanium dioxide semiconducting photocatalysts have optimal conversion efficiencies in the nanoparticle sizes. At such small sizes though, however, detrimental recombination of electrons and holes pairs occur more frequently on the surface of the particles. As such, there is expected to be an as-of-yet undetermined optimal particle size for photoplatinizing, where quantum effects gains are balanced with surface recombination losses. Models currently exist that predict the effect of gas-phase deposition conditions on thin film characteristics, but many of these conditions have yet to be experimentally verified. In this work, we demonstrate the effect that different process conditions have on the physical and mechanical characteristics of the thin film. Titania films were created via Dip-Coating (DC), Precursor-Vapor Deposition (PVD) and Flame Aerosol Deposition (FAD) onto stainless steel. The effect of various process conditions on the morphology of the film was explored by AFM, SEM, and XRD. Fractal dimensions were calculated from AFM images, and correlated to the film deposition conditions. Distinct variations were observed in the resultant fractal dimensions (ranging from 2.59 to 2.76) based on the deposition procedure and process parameters. DC led to the simplest films composed of unoriented primary particles. These films had the lowest roughness and the least fractal dimension. PVD led to particles of inhomogeneous size and shape that covered the surface in an uneven manner. FAD was carried out in various configurations and flow rates, resulting in quite different morphologies, ranging from long chain-like aggregates similar to diffusion-limited cluster-cluster growth, to dense aggregates resembling reaction-limited particle-cluster growth. Increased oxidizer flowrate resulted in fewer large spheres, but an increase in the number of smaller primary particles. An increase in dilution also produced larger primary aggregates due to the size and increased the number of primary particles participating in aggregate formation. Transient photocurrents were measured under different bias voltages to ascertain if there is any effect that these different physical properties have on the catalytic action of the films. Films with the best photocurrents were placed in a two-compartment, three-electrode photochemical cell and illuminated. Rates of hydrogen production were measured with a GC and correlated to the morphology of the films.
O3.40
Abstract Withdrawn

O3.41

Many of the biosensors developed from conjugated polymers thus far operate in solution. We focus on examining the potential of thin films as sensory platforms to biodetection strategies. The three-dimensionality afforded from thin films of non-aggregating poly(phenylene ethynylene) (PPE)s allows for favorable π-π interactions between polymer chains which leads to efficient exciton transport to yield greater sensitivity versus the one-dimensional transport in solution. The sensing mechanism occurs via electron transfer from the PPE to an electron-deficient small molecule quencher which have been shown to form a static complex. However, surface to volume ratio. However, when the dimensions of a given introduces challenges in tailoring these interactions. We have investigated the role of hydrophobic in quencher-film association through molecular structure design and optimization to provide high fidelity to the film, 1-2 atomic layers thick, on nanoscale devices. The optical properties of the titania demonstrate high catalytic activity, and the catalytic activity drops down when the size of the particles increases. First-principles calculations performed for a large ensemble of gold clusters of different size and shape demonstrate a clear statistical correlation between the coordination of gold atoms at the surface of the cluster and the reaction barrier for the CO oxidation, as observed experimentally. The catalytic performance of a gold nanoparticle is dictated by the interplay between the binding energy of the CO and oxygen molecules to the cluster, the surface migration barrier of the oxygen molecule, and the reaction barrier of the CO oxidation. X-ray absorption near edge spectra (XANES) measurements for first-principles calculations do not show any significant oxidation of Au clusters in the most catalytically active state. The binding energy of a gold nanocluster to the substrate (and the whole CO oxidation catalytic process) does not depend significantly on the type of the titanium oxide substrate (anatase, rutile, etc.) and depends on the number of oxygen vacancies on the oxide surface to which the gold atoms of the cluster bind. Reactive undercoordinated titanium atoms populated at the substrate surface near the gold cluster appear to assist in stretching the oxygen molecules thus lowering the reaction barrier even further.

SESSION O4: Catalysis II
Chairs: Valeri Petkov and Chuan-Jian Zhong
Tuesday Morning, November 29, 2005
Room 200 (Hynes)

8:15 AM O4.1

It is generally believed that the chemical activity of metal catalysts would be increased at the nanoscale because of the increment of surface to volume ratio. However, when the dimensions of a given metallic cluster are reduced to a few hundred of atoms, the electronic structure changes, as compared to the bulk, and thus its chemical properties are expected to change. Therefore, whether small metal nanoparticles remain good catalyst or are better catalysts than bulk materials remains an open question. Cobalt nanocrystals display a wealth of interesting size-dependent structural, magnetic, electronic, and catalytic properties. The structure of cobalt clusters undergoes several transformations as the number of atoms, while cobalt is ferromagnetic in the bulk, the magnetic moment per atom increases as the size of the cluster is reduced. Bulk cobalt surfaces are known to catalyze important chemical reactions in the Fisher-Tropsch process (that converts CO and H2 into olefins and paraffins). In this presentation we report ab-initio calculations on cobalt clusters with chemisorbed CO molecules. We investigate the changes in the structural and magnetic properties of pristine cobalt clusters upon CO chemisorption. Our results show that both binding energies of CO to 13-55 atom (0.5-1.5 nm) cobalt nanoparticles and preferred chemisorption sites depend on the cluster structure (whether fcc oricosahedral), size, and surface coverage. In addition we find a strong influence of CO on the magnetism of the cluster, leading to magnetic moments smaller than the bulk value, at variance with pristine clusters which have magnetic moments larger than the bulk. Our findings point at important changes in catalytic properties of cobalt at the nanoscale. We find that cluster size and surface coverage are two possible parameters to vary in order to control the Fisher-Tropsch synthesis.

8:30 AM O4.2

This presentation will focus on the development of new materials for fuel cell applications with emphasis on ordered intermetallic phases as both bulk electrodes and nano-particles. The use of high throughput combinatorial methods and nano-structured materials will also be discussed.

9:00 AM O4.3

Nano-sized gold clusters or very thin gold layers on titania oxide support are very active catalysts for the oxidation of carbon monoxide even below room temperature. Here we use aberration-corrected Z-contrast scanning transmission electron microscopy to show that 1-2 nm size gold particles, 1-2 atomic layers thick, on nanoscale titania oxide demonstrate high catalytic activity, and the catalytic activity drops down when the size of the particles increases. First-principles calculations performed for a large ensemble of gold clusters of different size and shape demonstrate a clear statistical correlation between the coordination of gold atoms at the surface of the cluster and the reaction barrier for the CO oxidation, as observed experimentally. The catalytic performance of a gold nanoparticle is dictated by the interplay between the binding energy of the CO and oxygen molecules to the cluster, the surface migration barrier of the oxygen molecule, and the reaction barrier of the CO oxidation. X-ray absorption near edge spectra (XANES) measurements and first-principles calculations do not show any significant oxidation of Au clusters in the most catalytically active state. The binding energy of a gold nanocluster to the substrate (and the whole CO oxidation catalytic process) does not depend significantly on the type of the titanium oxide substrate (anatase, rutile, etc.) and depends on the number of oxygen vacancies on the oxide surface to which the gold atoms of the cluster bind. Reactive undercoordinated titanium atoms populated at the substrate surface near the gold cluster appear to assist in stretching the oxygen molecules thus lowering the reaction barrier even further.

9:15 AM O4.4

A general approach combining synthesis, characterization and reactivity studies for the design of heterogeneous catalysts incorporating monodisperse metal nanoparticles into mesoporous oxide frameworks has been developed. These materials possess metal nanoparticles of nearly the same size and due to this unprecedented uniformity, intrinsic catalytic activity and selectivity behavior is measured rather than ensemble average kinetic behavior enabling accurate structure-function correlations to be developed. Monodisperse Pt nanoparticles of 1.7-7.1 nm were synthesized by alcohol reduction methods using poly(vinylpyrrolidone) (PVP) as a surface regulating agent. Pt particles of well-defined size were also synthesized in refluxing ethylene glycol (EG) using sacrificial metal ions. The addition of Pt precursors to refluxing EG solutions containing PVP and Ag ions at different concentrations led to the formation of cubic, cuboctahedral or octahedra. Spherical and faceted Pt nanoparticles were encapsulated into mesoporous oxides by in-situ hydrothermal synthesis. The resulting Pt/SBA-15 catalysts were characterized by a number of physical and chemical techniques. In order to expose the Pt surface, PVP and template polymer were removed by oxidation-reduction cycles at temperatures between 473 and 673 K. Thermogravimetric analysis has shown that polymers decompose over a wide temperature range. A high temperature ligand exchange method on faceted nanoparticles was used to replace PVP from the nanoparticle surface and replace with a long chain amine. Characterization of the catalysts by selective gas adsorption, ethylene hydrogenation and infrared spectroscopy confirmed that the polymers were removed by both pretreatments. Particle size effects on catalytic activity were probed with ethane hydrogenolysis, a structure sensitive reaction. Higher activity on smaller Pt particles suggested that coordinatively unsaturated surface atoms are more active than highly coordinated atoms. Hydrogenation/dehydrogenation of ethane and n-butane hydrogenolysis was used to probe the influence of particle size on reaction selectivity. Selectivity to benzene increased with decreasing particle size due to a decrease in the activation energy for benzene formation. Further hydrogenolysis of the propane (and ethane) of butane hydrogenolysis increased on smaller particles in agreement with ethane hydrogenolysis results. The influence of particle shape on intramolecular reaction selectivity was probed with the hydrogenation of α,ω unsaturated aldehyde.
Experimental observations have shown that larger Pt particles are more selective for the formation of the unsaturated alcohol. This study emphasizes the importance of Pt particle size, Pt3d electronic structure characterization and reactivity studies. The precise control obtained in these structures may enable the development of very accurate structure-activity and selectivity correlations in heterogeneous catalysis.

9:30 AM Q4.5
Quantitative Study of Au and Pt Catalytic Clusters by STEM and HRTEM. Xu Guo1, Laurent Menard2, Huiping Xu3, Shangpeng Gao3, Lin-Lin Wang4, Anatoly Frenkel4, Ralph Nuzzo4, Duane D. Johnson5 and Judith C. Yang1; 1Department of Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; 2Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; 3Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; 4Department of Physics, Yeshiva University, New York, New York.

The highly dispersed metal (e.g. Au) clusters have exhibited exceptional catalytic activity for several reactions, including CO oxidation [1]. Their high catalytic activity has been attributed to clusters' nano-structural effects (including cluster thickness, shape, chemical information, and number of atoms of the cluster). The three-dimensional exact structure and chemical bonding state of these supported clusters is still challenging to be quantified by conventional methods due to the limitations in understanding size distribution of supported metal clusters that are usually less than 1 nm (<100 atoms). Quantitative Z-contrast (or high-angle (>90 mrads) annular dark-field, HADF) imaging in a scanning transmission electron microscopy (STEM) technique can determine the exact number of atoms in a cluster by quantification of the absolute image intensity [2]. We have previously determined the number of atoms in very small clusters such as Pt5 and Pt7 in this [3, 4]. In this work, in order to understand the 3D structure and dynamics of the supported metal clusters, the quantitative HAADF imaging and high-resolution transmission electron microscopy (HRTEM) of the ligand-protected Au and Pd2Au2 supported Pt clusters are performed. We aim to measure the number of the Au and Pt atoms (13 – 100) and propose their 3-dimensional supported structure [1]. M. S. Chen, D. W. Goodman, Science, 306, 252 (2004); 2. J.C. Yang, S. Bradley and J.M. Gibson, Nanoletters, 3, 1147 (2003); 3. S. Bradley, J.M. Gibson, Materials Characterization, 51, 101 (2003); 4. A. Singhal, J.C. Yang and J.M. Gibson, Ultramicroscopy, 67, 191 (1997); Supported by the Department of Energy (#DE-FG02-03ER15475).

10:15 AM Q4.8
Three-Dimensional Structure of Metallic Nanoparticles from High-Energy X-ray Diffraction and Atomic Pair Distribution Function Analysis. Valeri Petko, Department of Physics, Central Michigan University, Mt. Pleasant, Michigan.

Knowledge of the atomic-scale structure is an important prerequisite to understand and predict the properties of materials, including the catalytic and optical ones. In the case of crystals it is obtained from the positions and the intensities of the Bragg peaks in the diffraction patterns. However, when the materials are made of nanoparticles, lack the translational symmetry and long-range order of usual crystals. The diffraction patterns of such materials only show a few Bragg peaks, if any, and a pronounced diffuse component. This poses a real challenge to the usual techniques for structure characterization. The challenge can be met by employing the so-called atomic Pair Distribution Function (PDF) technique and high energy x-ray diffraction. This non-traditional experimental approach takes into account both Bragg and diffuse scattering and yields the atomic structure in terms of a small set of parameters allowing the exploration of structure-property relationship. The basics of the technique will be introduced and its potential demonstrated with results from recent structural studies on iron-palladium nanoparticles and dendrimer stabilized gold nanoparticles in water.

ACKNOWLEDGMENT. The work was supported by NSF through grant DMR 0804391(NIRT).

10:30 AM Q4.7
Enhanced Charge Transport in Oxide Nanoarchitectures via Bonded and Conducting Phases. Debrah A. Bolling1, Michael S. Doescher2, Christel Lavery-Robert2,2, Jeffrey W. Long2, Jeremy J. Pietron1, Charles A. Edmondson3, Katherine A. Pettigrew4-4 and Rhonda M. Stroud4; 1Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia; 2CNRS-UMR 5508, Université Paul Sabatier, Toulouse, Cedex 4, France; 3Physics Department, U.S. Naval Academy, Annapolis, Maryland; 4Sensors and Materials, Naval Research Laboratory, Washington, District of Columbia.

Sensing and catalysis are rate-critical applications that require facile transport of analyte, reactant, or solute for high performance [1]. Aerogels and amibngs, which are sol-gel-derived ultrananoarchitectures, unite high porosity with material design freedom for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of molecules. Response times to gas-phase analytes are >100 times faster than those of the same chemistry expressed in a xerogel [2,3]. We now find that these pore-solid nanoarchitectures impose electrical pathways that yield macroscopic diffusion lengths for ions in conductometric sensors from room temperature to 600°C. The impedance of electrically conductive oxide nanoarchitectures markedly decreases with respect to the same material in crystalline nanoarchitectures. In MnO2 amibgels with <20-nm pores, proton wires with macroscopic lengths form upon exposure to humid atmospheres as water layers adsorb at the solid framework, enhancing the sensitivity factor for humidity by 14-fold relative to particulate films of nanocrystalline MnO2. Alternatively, grinding the amibgel into a powder to form a nanoparticulate film disrupts the continuity of the proton wire and enhanced electrical conductivity (and sensitivity to relative humidity) is not observed. Ceria aerogels exhibit higher oxygen-ion conductivity and more rapid spectral response to changes in the partial pressure of oxygen relative to nanocrystalline CeO2. In both ambient and high-temperature usages of these oxide nanoarchitectures, it is the bonded transport pathways inherent to the bicontinuous pore-solid networks of these nanoarchitectures that impart optimal electrical response. [1] D.R. Rolison, Science 290 (2000) 1698. [2] N. Leventis, I. Elder, D.R. Rolison, M.L. Anderson, C.I. Merzbacher, Chem. Mater. 11 (1999) 2837. [3] J.M. Wallace, J.K. Rice, J.J. Pietron, R.M. Stroud, J.W. Long, D.R. Rolison, Nanolett. 3 (2003) 1463.

11:00 AM Q4.8
Density Functional Theory Modeling of Bimetallic Nanoclusters for PEM Fuel-Cell Cathode Electrocatatysis. Lifang Lian1, Xiaofeng Qian2, Christos J. Fotoulis2, Kwei-Shen Yip2 and Jinghui Zhon2; 1Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio; 2Department of Nuclear Science and Engineering, MIT, Cambridge, Massachusetts.

We study Pt-(W,Ni,Ti,Au) bimetallic nanoclusters with up to 55 atoms using density functional theory. The structural stability and chemical ordering of these clusters are analyzed by correlating with the underlying electronic structure, using the newly developed quasimolecular orbital (QUAMO) analysis. The oxygen reduction reaction pathways near different sites are calculated in vacuum, and in aqueous environments with explicit water. The dependences of the activation energies on local electric fields are investigated.

11:15 AM Q4.9

While bulk Au is inert, Au particles approximately three nanometers in diameter are highly efficient at converting CO to CO2 even at room temperature (1). Diameter is not the only important dimensional variable: ultrathin Au films, CO2, also catalyze CO oxidation, and it has been found that a 4/3-monolayer Au thickness exhibits maximum catalytic activity (2). This remarkable behavior has inspired great interest in the area of size-dependent properties of gold nanostructures in catalyzing not only CO oxidation, but also numerous other important chemical reactions, including water gas shift and NO2 reduction (see, e.g., Ref. (3) and references therein). However, the reasons responsible for the size-dependent catalytic behavior of Au remain unknown, and most probes are unable to provide the atomic-scale resolution needed for such understanding when the experiment is carried out at typical catalyst operating pressures and temperatures. In this work, we employ a novel in situ method for studying gas-solid heterogeneous catalysis, using the highly brilliant x-rays of the Advanced Photon Source (APS) for characterizing the atomic-scale structure of both the Au catalysts and the oxide supports during CO oxidation. A quartz-walled deposition system that allows controlled gas flows from atmospheric pressure to 10-7 Torr has been specially constructed to mount onto a six-circle diffractometer at the APS. This unique apparatus enables both sub-monolayer control of Au catalyst deposition onto oxide supports and in situ monitoring of subsequent CO/O2-Au reaction. These two reactions are varied by using either TiO2(110) or TiO2-terminated SrTiO3(001) single-crystal supports. Reaction products are detected with a residual gas analyzer, and a substrate heater allows both the growth and reductions to be carried out at temperatures from 25 to 1000 °C. We present initial results on the structure and catalytic activity of Au nano-islands as functions of thickness and lateral dimension. 1. M. Haruta, Catal. Today 36, 153 (1997). 2. M. S. Chen, D. W. Goodman, Science 300, 252 (2004). 3. R. Meyer, C. Lemire, S.
In fuel cells, catalytic activity and utilization efficiency of catalyst should be simultaneously improved. Size reduction of catalyst is effective to improve catalytic mass activity. In general, carbon supports with high specific surface area are used to obtain fine Pt and PtRu catalysts. However, many micropores exist in carbon supports with high specific surface area. Catalysts burn in the micropores lose their opportunity to contact with polymer electrolyte and fuels, which results in becoming dead catalysts. In this paper, a new method reducing size of PtRu catalyst by addition of non-metallic elements is proposed. PtRu catalyst was synthesized by polyol process using ethylene glycol as reducer. Mixture of carbon support, Pt and Ru precursors and ethylene glycol was refluxed at 473 K for 4 hours with mechanical stirring under nitrogen atmosphere. Performance of direct methanol fuel cell (DMFC) was measured under passive state at 288 K with fuels of 15 wt.% methanol and ambient air. Loading amount of catalyst was 5 mg/cm² for both anode and cathode. B, S, N, P and Si were selected as additives of non-metallic elements. It was found that addition of S, N and P reduces size of PtRu catalyst and that P is most effective additive. Size of PtRu catalyst was reduced in 2 nm and dispersion of PtRu catalyst was also improved by addition of P. Heat of mixing of Pt-Pt and Pt-Pt bonding by P is to be cause of size reduction in PtRu catalyst by addition of P. HRTEM observation and TEM-EDX, XPS, XRF and XRD analyses suggested that P exists on surface of PtRu catalyst as oxide state. Maximum power density of DMFC was improved from 38 mW/cm² to 64 mW/cm² by using 2 nm of well-dispersed PtRuP catalyst. The other feature of PtRuP catalyst is retention of its size in 2 nm regardless of specific surface area of carbon support. PtRuP catalyst was synthesized by using carbon supports with specific surface area of 800 m²/g, 254 m²/g and 140 m²/g, respectively. TEM observation showed that size of these PtRuP catalysts is retained in 2 nm. Maximum power density of DMFC was improved by using PtRuP catalyst loaded on carbon supports having lower specific surface area. Carbon supports with lower specific surface area are less porous carbon supports. Usage of less porous carbon supports raises number of PtRuP catalyst existing on surface of carbon supports, which improves utilization efficiency of PtRuP catalyst. 2 nm of well-dispersed PtRuP catalyst loaded on less porous carbon supports is a strong candidate for achieving high catalytic activity and high utilization efficiency of catalyst simultaneously.

Monolayer Protected Clusters. Frank Zamborini 1 and Francisco Ibáñez 2; 1University of Louisville, Louisville, Kentucky; 2Chemistry, University of Louisville, Louisville, Kentucky.

In this talk we will describe the stability, conductivity, and vapor sensing properties of microcontact-printed films of 1.6 nm average diameter gold monolayer protected clusters (C6 Au MPCs). The C6 Au MPCs were stamped into parallel lines (~1.2 \m  wide and 400 nm tall) across two Au electrodes separated by a 1 \m gap. The chemiresistive vapor sensing properties were measured for saturated toluene and isopropanol vapors. As expected, patterned Au MPC films were unstable in the presence of saturated toluene vapors and their current response was non-reversible. Chemically linking the films with vapor phase hexanediol greatly improves their stability and leads to reversible responses. The extent of Au MPC cross-linking varies with different exposure times to diethyl vapor. Short exposures exhibit the highest response towards organic vapors, which is likely due to greater film flexibility. The conductivity of the films varies as a function of the temperature of the Au source (200, 320 oC), which correlates with the loss of organic material as measured by FTIR spectroscopy and the change in thickness and width of the film as measured by atomic force microscopy (AFM). The vapor sensing properties vary with temperature, conductivity, and organic content in the film, which are all inter-related. Reducing the size of vapor sensing devices based on Au MPCs is important for creating highly portable devices that can simultaneously detect many different analytes. This work demonstrates a simple method for reducing the size of such devices down to the microscale and describes some methods for maximizing the response.

Adsortive and absorbative materials are key elements in a variety of sensing and separation methods for laboratory and field analytical chemistry. Nanomaterials and nanostructured materials offer new opportunities in interactive sorptive methods in these applications. Such materials can offer many potential advantages such as increased surface area, exceptional volumetric densities of functional groups, and assembly into structures with nanometer linear dimensions from one another. In this paper, we examine the use of monolayer protected gold nanoparticles as sorptive layers for chemical vapor sensors and gold chromatographic separation applications. The sorptive properties of these materials are compared with those of more conventional polymers, and these results are used to draw conclusions about the relative roles of sorption and transduction in the detection limits reported for nanoparticle coated chemiresistor sensors. In addition, we have discovered that these sorptive materials also make excellent phases for capillary chromatography and capillary chromatography with angular channels.


The (1-x)alpha-Fe2O3-xSnO2 nanoparticles system has been obtained through a hydrothermal route under relatively mild conditions of temperature and pressure (200 C and 15 atm). Structural and magnetic characteristics of tin-doped hematite system are investigated by X-ray diffraction (XRD) and transmission Mossbauer spectroscopy. The mean particle diameter decreases from 70 to 6 nm as tin molar concentration increases up to x=1.0. The Rietveld structure refinement of the XRD spectra at low tin concentration are consistent with the presence of Sn4+ in the alpha-Fe2O3 structure in two different sites: substituting for Fe3+ in octahedral sites (0, 0, z) and occupying some interstitial sites (0, 0, 0) normally vacant in the hematite structure. At greater tin contents, a tetragonal SnO2 structure crystallizes, where the Fe3+ ions partially substitute for Sn4+ ions in the structure. A phase separation of alpha-Fe2O3 and SnO2 was observed for x>0.4: the alpha-Fe2O3 structure containing tin decreases simultaneously with the increase of the SnO2 phase containing substitutional iron atoms. The Mossbauer spectra were analyzed with a hyperfine magnetic field distribution, in which the distributions at lower magnetic fields can be assigned to lower spin density at Fe3+ in the vicinity of Sn4+ magnetic versus paramagnetic phase (quadrupole doublet) in the nanoparticle system of tin-doped hematite was determined from the Mossbauer spectra and studied as a function of composition. From XRD and Mossbauer results, the estimated solubility limits are x<0.2
for Sn4+ in the alpha-Fe2O3 and x>0.7 for Fe3+ in SnO2. This work is the first report on the hydrothermal synthesis and microstructure characterization of Fe4+/Fe2O3/Nb2O5. Introducing field effect modulation in micro/nano fluidic systems in a three-terminal device would enable the manipulation of ionic and molecular species at a similar level and even logic operation. Due to strong Debye screening, field effect control in ionic solutions has to be occurring in nanoscale. Here we report the integration of chemically synthesized inorganic nanotubes into metal-oxide-solution field effect transistors (MOSolFETs) which exhibit rapid field effect modulation of ionic conductance. Surface functionalization, analogous to doping in semiconductors, switches the nanofluidic transistors from p-type field effect transistors (p-FETs), to ambipolar FETs, and n-type field effect transistors (n-FETs). Ambipolar behavior is of particular interest in the expression/Boltzmann model.


To address the interplay between surface properties and electron transport in metal oxide nanowire sensors we have applied an array of imaging techniques based on electron and scanning probe microscopies. In particular, the synchrotron based X-PEEM imaging of the wired nanostructure we were able to acquire the NEXAFS spectra from the surface of individual TiO2, SnO2 and SnO2 nanowires thus opening a new avenue to visualize and spectrally address the dynamic surface phenomena on the individual nanostructures both in real time and at nano- and mesoscopic level. These results were complemented with SEM-EBIC measurements on chemi-FET based on individual n-type semiconducting oxide nanowires. The particularities of the electron transport in the realistic device were studied as a function of gate potential and in presence of contact effects.

Macroscopic Fibbers of Oriented Vanadium Oxide Nanoscopic Ribbons: Application toward High Sensitive Alcohol Micro-Sensor. Renal Baccot1, Lahire Biete1, Florent Carn1, Maryse Mauguy2, Marie-Francoise Perrier2 and Jacques Livage2; 1CRPP-CNRS/Universite Bordeaux-I, Pessac, France; 2LCMC/ Universite Paris VI, Paris, France.

Shaping inorganic materials is a new topic of research that encompasses both the areas of soft matter and soft chemistry. In this issue sol-gel process can be associated to metastable thermodynamic systems (air-liquid or bilique foams) to design new macrocellular materials. As discussed below the macroscopic pattern can be substituted by a shear process that allows reaching one dimensional (1D) materials. Among inorganic polymers, extensive interest is focused on vanadium oxides mainly for their structural diversity and potential applications in various domains as for instance, heterogeneous catalysis, cathode materials for advanced lithium batteries, visible light photocatalysis and electro-chromic devices. In this specific concern that associates an extrusion process with vanadium oxide gel, first vanadium oxide macroscopic fibbers have been obtained[4] with longitudinal Young modulus around 15 GPa that corresponds to the values obtained for carbon nanotubes fibbers. Those vanadium oxide fibbers depict strong high scale textural anisotropy as observed through cross-polarized microscopy. TEM observations and SAXS experiments reveal that those macroscopic fibbers are made of macroscopic nanobands organized with a preferential orientation parallel to the macroscopic thread main axis. These fibbers allow fast cycling insulator-semiconductor microelectrodes directly related respectively to the absence or presence of an alcohol vapor source, acting as a highly sensitive and fast alcohol micro-sensor. For instance, they can detect down to 0.1 ppm of alcohol vapor within 18 seconds at 40°C. 1- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, E. Sellier, M. Birot, R. Backov J. Mater. Chem., 2004, 14, 1370, 2- F. Carn, A. Colli, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov Adv. Mater., 2005, 17, 62, 3- F. Carn, A. Colin, M.-F. Achard, R. Backov Adv. Mater., 2004, 6, 140, 4- L. Biete, F. Carn, M. Mauguy, M.-F. Achard, N. Steunou, J. Livage, R. Backov Nature Materials (submitted).

Doping and Transient Responses in Single Nanotube Nanofluidic Transistors. Rong Fan1, Min Yue2, Rohit Karnik2, Arun Majumdar2 and Peidong Yang2; 1Department of Chemistry, University of California, Berkeley, California; 2Medical Engineering, University of California at Berkeley, Berkeley, California.

The ability to manipulate charge carriers (electrons and holes) in
SESSION 06: Poster Session: Nanoparticles and Nanostructures in Sensors and Catalysis II
Chairs: Wayne Daniell, Valeri Petkov and Chun-Jian Zhong
Tuesday Evening, November 29, 2005
8:00 PM
Exhibition Hall D (Hynes)

O6.1 Structure Determination of Small Metal Clusters by Density-Functional Theory and Comparison with Experimental Spectroscopic Spectra Christian Bichuch1, Andre Fiebig2, Joerg Behler1, Matthias Scheffler2, Gert von Helden2, and Gerald Meijer2; 1Department of Chemistry, Christian-Albrechts-Universität zu Kiel, 2Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.

Small metal clusters or nano-particles exhibit properties that are often quite different from those in the bulk phase. For example, small metal clusters have been shown to exhibit unusual magnetic properties. Small metal clusters also play an increasingly important role in catalysis. Therefore, it is paramount to gain a better understanding of the atomic structure and properties of small metal clusters. The size-specific far-infrared vibrational spectra for charged vanadium clusters as well as charged and neutral niobium clusters with sizes between 3 and 24 atoms have been measured using infrared multiphoton dissociation. Using DFT calculations, we calculated the ground state energy and vibrational spectra for a large number of stable and unstable clusters. Comparison of the calculated vibrational spectra with those obtained in the experiment allows us to deduce the cluster size specific atomic structures.

O6.2 Electron Energy Loss Spectroscopy Study of Monolonic and Cubic Rare Earth Oxide Nanoparticles. Ashley S Harvey, Bing Guo, Ivan M. Kennedy, Subhash H. Rishbud and Valerie J. Leppert; 1Chemical Engineering and Materials Science, University of California, Davis, California; 2Mechanical and Aeronautical Engineering, University of California, Davis, California; 3School of Engineering, University of California, Merced, California.

Rare earth oxide (REO) nanoparticles (NPs) are versatile materials with applications ranging from catalysis, sensors, and fuel cells to nanophosphors for light emission and plasma displays. The acid-base chemistry of the surface transport properties of REO-NPs lead to desirable catalytic properties, particularly for the oxidative coupling of methane, with the added feature of high thermal stability. Bulk properties are in turn greatly influenced by the nanostructure of the REO-NPs, which we have characterized in the present work by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). These state-of-the-art characterization tools were used to distinguish structural details for cubic and monoclinic crystal phases of heavy metal REO NPs synthesized by a flame combustion process. Specifically, we examined the EELS oxygen K-edge for Ho, Tm, Er, and Yb sesquioxides in both phases. The energy loss near edge structure (ELNES) of the oxygen K-edge differs substantially for each phase. We observed the usual double-peak structure seen in EELS for oxygen atoms tetrahedrally surrounded by metal atoms, with the peak separation greater for the cubic structure than the monoclinic. Also, a trend of increasing peak separation with increasing atomic number was noted for a series of REO-NPs. Our results show how EELS can be utilized to reveal subtle structural differences between nanoparticles that crystallize in the common cubic structure and those that form in the less common monoclinic structure.


It is well known that the size, shape, and composition of nanostructures dictates their physical and chemical properties. The relationship between physical dimensions and material properties emphasizes the significance of fully characterizing these nanostructures, and highlights the role of this characterization in both fundamental science questions and future technological applications based on nanomaterials. We report the synthesis and optical characterization of monodisperse crystalline gold nanoparticles that has allowed us to identify higher order surface plasmon resonance modes associated with these structures. The identification of higher order surface plasmon modes is important because it provides not only a greater understanding of their physical properties but also a spectroscopic fingerprint that can be used to characterize and assess the quality of such structures. The nanoparticle structures were generated by a surfactant mediated, three-step seed growth process with a relatively homogeneous size distribution. The purity of the nanoprisms has allowed us to observe a weak quadrupole resonance in addition to the strong dipole resonance which are characteristic of the nanoparticle structures. The experimental optical spectra agree with discrete dipole approximation calculations that have been modeled from the dimensions of gold nanoparticles produced in this synthesis.

O6.4 Abstract Withdrawn


We report significant improvement in the production rate and yield of single-wall carbon nanotube (SWNT) materials produced by a re-designed arc discharge synthesis system. The traditional bell-jar geometric design was replaced with carefully designed arc-processed graphite rods within a 7 x 5 cm quartz tube. The confinement of the AC-arc and the resultant variation in the thermal profile within the chamber results in an as-produced homogeneous soot with greater proportions of SWNTs than those produced by traditional DC-arc discharge systems. Conditions can be tailored such that the as-produced SWNT soot is very closely related to those materials produced by laser vaporization systems in tube helicity, diameter distribution and defect content. This improves the ability to tailor specific nanotube compositions that are application specific. Overall, a range of experimental parameters were varied in this new system design in order to establish the optimum synthetic conditions including carbon type, particle size, gas composition and current level. The highest quality as-produced soot was generated at rates up to 1 gram/hour, with a gravimetric SWNT content greater than 50% w/w and a Raman G/D ratio of 280. The results from parameter variation and a discussion of optimum conditions will be presented.

O6.6 Surface Plasmon Excitation in Three-dimensional, Ordered, Gold Nanocrystal Arrays Using a Prism Coupler. Kai Yang, Hongyou Fan, Michael J. O’Brien, Kevin J. Malloy, Gabriel P. Lopez, Jeffrey Brinker, Mansoor Sheik-Bahae, and Thomas W. Simmon; 1Center for High Tech Materials, University of New Mexico, Albuquerque, New Mexico; 2Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; 3Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; 4Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico.

Surface plasmons (SPs) in thin film metals have been extensively studied by physicists, chemists, materials scientists and biologists for decades. Today, surface plasmons are being explored for a wide range of applications in optical storage, signal processing, microscopy and nonlinear devices, as well as being used to construct sensors for detecting bio-molecules. Recent advances in nanotechnology now allow metals to be structured and characterized on the nanometer scale and incorporated into dielectric films. For instance, direct observation of water-soluble nanocrystalline gold micelles including their self assembly with silica into robust, ordered, nanocrystalline arrays in bulk or thin film forms has been demonstrated (Science, 304, 567-571, 2004). We study the properties of surface plasmon excitation in these new class of films and underlying science. In our effort we examine the optical properties of these 3-D ordered gold NC/silica arrays. These films are synthesized as described above. The gold nanoparticles are arranged in the silica host matrix in a face-centered cubic lattice with the mono-dispersion gold core size of 3 nm (variation less than 7%). We observed the collective optical behavior of the 3-D ordered gold NC array and find a blue shift in the plasmon absorption peak with increasing gold volume fraction (Au loading). Plasmon resonance bands centered at 536, 530, 520 nm are measured for gold NC arrays with a gold loading factor of 0.25, 0.5 and 1.0, respectively. The blue shifts results from plasmon excitation (collective oscillation of free electrons) of individual gold NCs mediated by coupling interactions with neighboring NCs. The plasmon generation in the 3-D ordered, gold NC/silica arrays is a result of using a prism coupler. The corresponding angular spectra of the gold NC films show the resonance angles at 66.4, 63.3, and 60.1 degree for gold loading factors of 0.25, 0.5 and 1.0, respectively. Modeling results based on a 3-layer model and experimental dielectric constants of the samples (obtained by ellipsometry) show the trend of the evolution of the angular spectra. The experimental results differ from those estimated using the effective media theory as a result of the plasmon enhanced local fields occurring near the gold nanoparticles.

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An electrospun carbon black-polymer fiber-based gas sensor. Yong Soon Kim1, Park Young Sung1, Park Byungwoon2, 1Electronics and Telecommunication Research Institute, Daeguon, South Korea; 2School of Materials Science and Engineering, Seoul National University, Seoul, South Korea.

Conductive carbon black-polymer composites have been used as a sensing element in electronic noses (Acc. Chem. Res. 37 (2004) 663). They are conventionally deposited by drop-coating well-dispersed composite solutions onto detection electrodes. However, this method has difficulties in achieving the homogenous distribution of carbon black particles in polymer matrix and uniformly thin films, which is very important to fabricate a reproducible sensor. This work describes a procedure for electrospraying for fabricating the carbon black-polymer composite sensors. A composite solution was injected through a needle under a strong electrical field, carbon black-embedded polymer fibers were formed as a result of electrostatic jetting. The average diameter of these composite nanofibers could be controlled by varying experimental parameters such as their concentrations in the composite solution, the strength of the electric field, and the feeding rate of the precursor solution. Compared with the conventional composites, the electrospun films were observed to have highly homogenous carbon black distribution and porous surface morphology, resulting from the condensed collectivity of randomly arranged carbon black-embedded polymer fibers. In addition, a film thickness was possible to control by means of the electrospraying deposition time over a selected sensing area. These nanofibrous features have improved the sensing properties of the composite sensors; the homogeneous and uniform characteristics provided good stability with respect to operation time and the high porosity induced fast response times.

Hydrothermal preparation and photocatalytic of titanium dioxide. Wen Ren1, Yi-Fun Xie2 and Chaochin Su1, 1Department of Chemistry, National Central University, Zhongli City, Taoyuan County, Taiwan; 2Institute of Organic and Polymeric Materials, National Taiwan University of Technology, Taipei, Taiwan.

Titanium dioxide (TiO2) is one of the most important semiconductors for photocatalytic application due to its strong oxidizing power of its holes, good photoelectric conversion rates. When a composite solution has been studied in detail. The photocatalytic activity of as-prepared TiO2 was tested in the reaction of methylene blue (MB) photodegradation in aqueous solution. The results show strong correlation between the structure parameters and photocatalytic performance of the TiO2 samples to the hydrothermal treatment conditions. The anatase TiO2 was successfully obtained at temperature as low as 150 °C. The anatase TiO2 was irregular but near elliptical in shape with average size of 15 ± 20 nm and well dispersed as observed by TEM. Hydrothermal treatment at higher temperatures and/or longer reaction time increases the tendency of crystal growth. The BET surface area decreased from 150 to 80 mg/g with increase of hydrothermal treatment time up to 24 hours at 200 °C. To study the thermal stability of anatase TiO2, calcination experiment was carried out at higher temperatures. A phase transformation from anatase to rutile (α → r) was observed at a calcination temperature of 700 °C and completed at 800 °C. The TiO2 powder became nebulous and conglomerated with undefined shape upon calcination. The photodecomposition rates of MB using hydrothermal samples are comparable to those of calcined samples at temperatures below 600 °C. For higher calcination temperatures, the MB photodecomposition becomes slower. These results indicate that the anatase phase of TiO2 dominates the experimental conditions. A plausible explanation is that the photocatalytic activity and the TiO202 oxidation condition is disturbed.

Active Pt Clusters from Dispersed Single Atoms on Carbon Nanotubes. Yong-Tae Kim1, Kazuyoshi Oshihama1, Koichi Higashimine2, Kazu Kato3, Tomoya Uruga3, Keiichi Osaka3, Kenichi Kato4, Masaki Takata4, Hiroshi Suematsu2 and Tadaoki Mitani3, 1School of Materials Science, Japan Advanced Institute of Science and Technology, Nomih, Ishikawa, Japan; 2Japan Synchrotron Radiation Research Institute /SP, Hyogo, Japan; 3Research for Evolutional Science and Technology, Japan Science Technology Cooperation, Kawaguchi, Saitama, Japan.

The discoveries of carbon nanomaterials such as C60 and nanotubes opened a new field of nanoscience and nanotechnology. One of the most attractive applications of carbon nanomaterials is in the enhancement of fuel cell performance based on nanoscience. Generally, since the energy of a fuel cell is produced via a reaction of the fuel gas or liquid on the electrolytically active material supported on carbon, the electrocatalyst is a key factor in determining cell performance. Also, the carbon supports largely affect the properties of the electrocatalyst, such as dispersity, size distribution, particle shape and size. The application of carbon nanotubes to electrocatalyst supports has been attempted to utilize their superior properties of high intrinsic conductivity, adequate specific surface area, accessible surface texture and electrical conductivity and have shown a high electrocatalyst performance compared with carbon black. There have been limitations, however, to produce small size and monodispersion of photocatalytic active materials on CNT. In order to improve the dispersity, chemical functional groups such as carboxylic, carboxyl, or phenol. In our study, we introduced a two-step process to provide a new formation method of clusters beyond the limitation mentioned above. This process includes: 1) Formation of a single-atom monolayer by the reduction of the Pt precursor (H2PtCl6) with NaBH4 on thiolated multi-wall carbon nanotubes (S-MWNT); 2) Formation of Pt clusters from single atoms by heat treatments at Th (Temperature of heat treatment) followed by slow quenching to R.T.. It was demonstrated, using TEM and X-ray analyses using synchrotron radiation on samples prepared from a reduction of a Pt precursor on thiolated multi-wall carbon nanotubes, that the surfaces of the carbon nanotubes were covered with a monolayer of single Pt atoms bonded to thiol groups. Removing the thiol groups by heat treatment at Th = 523K, an aggregation of single Pt atoms was started, and then reached a dynamically fluctuating state. Through slow quenching to R.T., monodisperse clusters, about 1 nm in size were formed. The monodisperse 1nm clusters showed the highest electrocatalytic activity for the methanol oxidation reaction. Moreover, a unique route enables to control a clusters size by setting heat treatment temperature; the size tends to increase with the raising of temperature. This phenomenon is attributable to the melting point drop of cluster. These clusters (or atoms) drift and meet on MWNT and coincidently melt into larger clusters. After some repetition of the above process, the growth of the clusters is finally limited by the cluster melting point, i.e. growth stops when it reaches Th. This is equivalent to controlling the cluster size by Th at an atomic scale.


Crystalline TiO2 (Anatase configuration) thin films are widely used in the photocatalysis and photovoltaic industries ([self cleaning surface and renewable energies for example]). The synthesis of these films is obtained from a dispersed solution of primary particles mixed with a sol-gel using Sol-Gel processes which allows the formation of TiO2 molecules inside inorganic network to create what is called hybrid materials. Spectroscopic ellipsometry is the technique of choice to characterise thickness and indices of these thin layers. The adsorption of vapor of organic solvents at room temperature by these porous materials is used to modify the refractive index of the layer. The change in refractive index induced by the introduction of solvent is measured by ellipsometry and calculated following the Lorentz-Lorenz effective medium model is used to calculate the wavelength of adsorption bands of the porosity at different pressures. Ellipsometric porosimetry (EP) measurements become an effective method for characterization of porosity, pore size distribution (PSD) and Young modulus of porous films. EP measurements accurately the pore size distribution and the porosity of the layer. In this paper, a detailed description of the ellipsometer will be exposed and several examples will be presented for micro-porous layers (with pore size lower than 10nm in radius) using the Dubin Rubin Radushkevich formula and meso-porous layers (with pore size larger than 1nm) using the Kelvin formalism. The porosity of the layer ranges from few percent up to 40%. [1] SORPAI, 26 rue P. Jouigneaux, 92270 Bois-Colombes, France.

Characterization of the surface of nanostructured zirconia-containing catalysts by ESR spectroscopy of O2 paramagnetic species. Natalya Y. Gnatyshyna, Alexander V. Zaitsev, Vladislav A. Sadykov and Alexander M. Volodin; Borskoy Institute
Oxide materials on the basis of stabilized ZrO2-CeO2 are widely used in chemical industry as construction materials, solid electrolytes with oxygen conductivity and catalysts for various oil processing reactions and nitrogen reduction by hydrocarbons in diesel engines exhausts. In the current study, we investigated the properties of materials: (1) materials containing separate zirconia nanoparticle with typical size 1-3 nm localized between the aluminosilicate layers of natural clays; and (2) materials containing mesoporous aggregates of ~5 nm zirconia nanoparticles within O2- radical anions generated by adsorption of hydrogen peroxide or NO+O2 mixture were used as spin probes for characterization of the nanostructured zirconia-containing catalysts by ESR. The concentrations of oxygen radical anions formed by H2O2 decomposition in the zirconia-pillared clays decreased with increasing metal cations appeared to exceed those of monolonic and cubic zirconia. Meanwhile, adsorption of the NO+O2 mixture on clays stabilized by ZrO2 nanoparticles did not lead to the appearance of O2- radicals. This result implies that the similar pillars in pillared clays are different from those of bulk zirconia. Nitrosyl complexes appear to be key intermediates in the formation of oxygen radical anions from NO+O2. They are known to be formed in significant concentrations on zirconia samples having strong Lewis acid sites. Nanoscale ZrO2 pillars apparently do not have such sites, and that is why oxygen radical anions are not formed from the NO+O2 mixture on them. Comparison of the O2- formation from NO+O2 over different crystalline modifications of ZrO2 has shown that monolonic zirconia has the highest specific concentration of surface sites where O2- radical anions are formed. This result agrees well with the observation that nitrosyl complexes are formed in highest concentrations over monolonic zirconia having the most significant distortions in the coordination sphere of zirconium cations. Thus, both similarities and significant discrepancies have been observed in the composition and concentration of oxygen radical anions for catalysts with significantly different composition and surface structure. The experimental results have been explained taking into account the literature data on the nature of active sites on studied catalysts and assuming two different mechanisms for generation of the O2- radical anions. If liquid hydrogen peroxide is used, the O2- radical anions are formed via an acid-base reaction with participation of terminal hydroxyl groups, whereas nitrosyl complexes appear to be key intermediates in the formation of NO and O2. The obtained results show that the used approaches can be recommended to be used for characterization of the surface properties of a wide range of oxidative catalysts containing zirconium cations. This work is supported by Zanar Bear International Charitable Scientific Foundation and Integration Project 8.23 of Presidium RAS.

O6.12 Non-lithographic Nanofabrication Using Porous Alumina Membranes. Bhargava Ram Kanchibotla1, Lu Tian2 and Latika Menon1
1Physics, Northeastern University, Boston, Massachusetts; 2Physics, Texas Tech, Lubbock, Texas.

We have used a non-lithographic nanofabrication method for fabricating nanoporous array templates directly on a substrate. The method is based on plasma etching through nanoporous alumina template grown directly on the substrate. A thin alumina template is first created on the substrate as-deposited by anodization. The resulting template consists of a hexagonal array of pores each ~50nm in diameter. Below the pores is a thin layer of barrier alumina followed by a layer of aluminum and the substrate. Reactive ion etching is carried out through the pores. By controlling the etch conditions, such as etch rate, power, etc., we have demonstrated highly anisotropic etching through the alumina and aluminum layer below the pores. In a similar process, we have also demonstrated the transfer of nanoporous alumina pattern to create an array of highly ordered pores on Si and GaN surface. Such nanoporous semiconductor surfaces will be used in the growth of novel semiconductor nanowire arrays for applications in biological and electronic applications.


Thin dielectric films with nanocrystallites are the most promising materials for the development of gas sensors toward low gas concentration in air. Whereas, their hydrogen sensitivity at low temperature is not satisfactory. Surface modification is an effective method to enhance sensitivity and selectivity of SnO2-based gas sensors. In this paper, a SnO2 film hydrogen gas sensor fabricated by a DC reactive magnetron sputtering on Si substrate was modified with Ni nanoparticles. The effects of Ni nanoparticles on hydrogen sensitivity of SnO2-based gas sensor were studied. Prior to and after different treatments including Ar+ sputtering, vacuum annealing, and heat treatment in oxygen environment for the SnO2 films with and without modification, chemical composition and surface microstructure of these films were verified by X-ray Photoelectron Spectroscopy (XPS) and Field-emitted scanning electron Microscopy (FESEM). The results show that the surface microstructure of SnO2 films is greatly influenced by different treatment methods. In addition, the nickel nanoparticles were distributed to the surface of Ni modified SnO2 film or permeate into the SnO2 film. The XPS analysis indicates that the binding energy of the chemisorbed molecular oxygen in the XPS core level spectrum is related to the amount of Ni. Chemisorbed oxygen sites will increase owing to the introduction of Ni2+ compared with unmodified SnO2 thin films. In addition, surface resistance of these films which is sensitive to chemisorption and reducing reactions is greatly controlled by the introduced Ni2+ with the help of chemisorption of the surface. Finally, the results indicate that the difference of gas-sensing properties of the Ni modified SnO2 film and unmodified SnO2 film is determined by their surface chemical composition and morphology. Compared with the unmodified SnO2 film, the Ni surface modified SnO2 film annealed in vacuum environment has the greatest sensitivity to 1000ppm hydrogen gas in dry air at relatively a low operating temperature, which can be ascribed to its rough surface and a great amount of chemisorption oxygen on its surface.

O6.14 Engineering Hierarchically Porous Films and Patches for SERS Substrates. Daniel Melvin Kuncicky1, Steven D. Christensen2 and Orlin D. Velev1
1Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina; 2Edgewood Chemical Biological Center, U.S. Army RDECOM, Aberdeen Proving Ground-Edgewood Area, Maryland.

Thin films of colloidal nanoparticles with controlled and reproducible structure could be an important element in sensors, water quality monitors, and in routine analytical practice. We have demonstrated that the combination of convective assembly and latex templating allows fabrication of highly efficient nanostructured substrates for surface-enhanced Raman spectroscopy (SERS)-based sensors. The structure-dependent performance of these SERS substrates was systematically characterized with cyanide in continuous flow milliliterous chambers. A matrix of experiments was designed to isolate the SERS contributions arising from nano- and microscale porosity, local ordering of the micropores, and the thickness of the nanoparticle layer. The SERS results were compared to the substrate structure observed by scanning electron microscopy (SEM) and optical microscopy to correlate substrate structure to SERS performance. The Raman peak intensity was consistently highest for nanoporous substrates with three-dimensionally ordered micropores, and decreases if the micropores are not ordered, or not templated. Removing the nanoscale porosity by fusion of the nanoparticles (without removing the large micropores) leads to drastic plunge in substrate performance. The peak intensity does not strongly correlate to the thickness of the nanoparticle films. At present, SERS substrates made by us or others are in the form of patches and strips of 1-10 micrometers. There is a range of nanoporous advantages that can be derived from making substrates in the form of arrays of sub-millimeter patches. We have recently discovered a modification of the technique that would allow making uniformly thick and well-structured to be made in batches. The new method is based on controlled drying of droplets from concentrated suspension on surfaces with intermediate hydrophobicity. We found that droplets of micrometer suspension deposited on partially hydrophobic polymer (of contact angle ca. 40-80 deg) do not dry by the accepted "coffee ring" mechanism. Instead, they begin shrinking, the particles inside begin crystallizing and the final result is a flat or slightly bulging patch of crystallized latex. If metallic nanoparticles are added to the droplet, latex crystal - gold nanoparticle patches of round flat shape, equivalent in structure to the SERS nanofilm substrates are formed.

O6.15 Sprayed Carbon Nanotube Thin Films as Hydrogen Sensors. Isabel Sayago2, Edgar Munoz2, Eva Terrado1, Manuel Alexiandre2, M. Carmen Horillo2, Jesus Lozano2, Jose Pedro Santos2, Esperanza Lafuente2, Wolfgang K. Masers1, Ana M. Benito1, Javier Gutierrez2, Ana M. Teresa Martinez1, Instituto de Carboquimica-CSIC, Zaragoza, Spain; 2Laboratorio de Sensores, IFA-CSIC, Madrid, Spain.

We present a novel, simple, and versatile method for preparing carbon nanotube-based hydrogen sensors. Single-walled carbon nanotubes (SWNTs) were ultrasonically dispersed in ethanol and sprayed on alumina substrates. Pd-functionalization of the employed SWNTs enabled the nanotube sensitivity to hydrogen. The fabricated thin film sensors exhibited good sensitivity at room temperature in reversible and reproducible hydrogen detection processes.
06.16 Synthesis of Noble Metal Nano-particles under Energetic Irradiation Fields. Nobuhiko Maeda1, Taiei Hiroki1, Fumioebu Horl,1, Shizuki Okuda1, Ryoeichi Taniguchi1, Tatsuo Kazuhara1, Tomoko Aoe2 and Akihito Iwasaki1; 1Osaka Prefecture University, Sakai, Japan; 2The Institute of Physical and Chemical Research (RIKEN), Saitama, Japan.

Dilute aqueous solutions with Au3+ only, Pd2+ only or Au3+ + Pd2+ ions and additives (PEG-MG; Polyethylene Glycol Monostearate or SDS/Sorbitan) are irradiated with 10 MeV electrons or 1.6 GeV carbon ions. For comparison, the solutions are also irradiated with ultrasound at 200 kHz. After the irradiation, the color of solutions is changed from buff yellow to deep red. The UV-vis absorption spectra show that after the irradiation, absorption around 530 nm appears, which corresponds to the excitation of the surface plasmon of Au nanoparticles. The result confirms that the irradiation reduces the noble metal ions in the aqueous solution, which synthesizes Au nanoparticles. Au nanoparticles are examined by using a transmission electron microscope (TEM). The average diameter of the nanoparticles is 50 nm for 1 MeV γ-ray irradiation, and 15 nm for 10 MeV electrons irradiation. This result suggests that the processes of solution reduction and nanoparticle synthesis strongly depend on irradiation conditions. From the results for γ-ray, electrons and heavy ions irradiations, the effects of irradiation parameter (total dose, dose rate, LET (Linear Energy Transfer) and so on) on nanoparticle synthesis are discussed.

06.17 Macroporous Cu2SnTi4O12 thin film sensors prepared by pulsed laser deposition on PMMA microsphere templates. Il-Doo Kim1,2, Anver Rothschild1, Takeo Hyodo3,4,5 and Harry L. Tuller1; 1Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; 3Department of Materials Science and Engineering, Nagasaki University, Nagasaki, Japan.

The pursuit of new materials with novel functionalities has led, over the past several years, to the use of silica and polymer microspheres as self-assembled building blocks for the fabrication of quasi-ordered macroporous structures. Various materials have been investigated, however, to employ this method to synthesize complex compounds reproducibly, largely due to the nature of the wet chemistry routes used to infiltrate the voids between the spheres with liquid precursors. In this present work, we demonstrate successful application of the microsphere templating strategy to the fabrication of macroporous Cu2SnTi4O12 (CCTO) films via pulsed laser deposition (PLD). Chemical and physical synthesis routes were combined to prepare macroporous structures of materials with complex compositions. This processing strategy can provide a simple and versatile means to produce ordered macroporous films of a wide variety of materials, especially inorganic materials, with ability to control parameters such as porosity, film thickness, composition, etc. as well as the ability to produce multi-layer structures of compounds with complex chemistry. Moreover, the ability to control the macroporous structure of such films on a different range of scales from 50 nm to 5000 nm will allow systematic investigation of microstructure-property correlations in different classes of materials. Due to their simplicity and versatility, the combination of these techniques, we believe, will open up new opportunities for processing novel materials with enhanced surface activity for applications in e.g. gas and chemical sensors, catalysts, and fuel cells.

06.18 Synthesis of Novel ZnO Nanostructures: Spheres, Sheets, Needles, Tipped Nanorods and Wires, Polyhedral Cages, Shells and Microphone Like Structures. Aurangzeb Khan1 and Martin E. Kordesch1,2; 1Physics and Astronomy, Ohio University, Athens, Ohio; 2CMSS Program, Ohio University, Athens, Ohio.

Novel ZnO nanostructures such as nanowires, nanoparticles, nano-cages, needles, shells and other shapes are synthesized via thermal evaporation of ZnO and graphite mixture in the presence of argon and nitrogen flow. The nanoparticles exhibit unique physical shapes and are hollow inside and their walls are composed of nanovoid and cathodoluminescence throughout the entire sample. Below 200 K show typical emission spectra of ZnO. These structures can be studied for various applications in optoelectronics and sensors.

06.19 Sequential Oxidation and Functionalization of Nanostructures: The Site-Specific Controlled Assembly of Different Nanoparticles on a Surface. Doan Wonter1 and Ulrich S. Scherf2,3; 1Max Planck Institute for Polymer Research and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; 2Dutch Polymer Institute (DPI), Eindhoven, Netherlands.

In this contribution the formation of nano-structures consisting of multiple differently sized nanoparticles is reported which is a crucial step towards the directed preparation of functional devices. The presented technique not only allows the formation of a monolayer into carboxylic acid groups which can, in a second step, be decorated with nanoparticles or used as templates for the attachment of an additional monolayer. The formation of ordered structures of nanoparticles is of importance e.g. for nanoscale interconnects, electronics and for bio-nano recognition applications. At the same time the controlled formation of 2D arrays of different nanoparticles is expected to contribute to the study and application of photoelectrochemical processes between semi conductive nanoparticles also in relation with the shape and size of the nanoparticles assembles. As the first example we present the preparation of nanostructures consisting of arrays of gold nanoparticles with a diameter of 5 and 20 nm. These particles may be placed on a surface with high spatial resolution with the aid of a closed-loop scanner system. The particles in turn may be used as nucleation sites for electrosynthesis deposition of gold or silver, before mentioned structures may be prepared by sequential local probe oxidation and surface modification processes. Existing structures on the surface will remain in tact during subsequent steps. If desired this method may be combined with dynamic plow lithography. In addition we will demonstrate the assembly of fluorescent ZnS/CdSe core/shell nanoparticles in well-defined structures on a wafer. Due to the nature of the probe oxidation process these patterns may be regular but also in various complex shapes. The assembled structures are visualized by means of confocal laser scanning microscopy. The presented technique is not limited to arrays of gold and CdSe/ZnS nanoparticles but also other particles may be used and even chemical modification routes known from SAM modification procedures may be applied.

06.20 Synthesis and applications of nanoparticles with photon upconverting properties. Peng Zhang1, Khoi Nguyen1, Damon Wheeler1, Amanda Bernauer2 and Suzana Rogelj1; 1Chemistry, New Mexico Tech, Socorro, New Mexico; 2Biology, New Mexico Tech, Socorro, New Mexico.

Photon particles have been used for decades in various applications. When ultraviolet light strikes the photon-coated area in a screen or bulb, it excites the particles and colored light is produced in a process called down-conversion. The opposite effect also exists, where a photon particle is excited with an infrared or red light (longer wavelength) and emits blue/green/yellow color (shorter wavelength). The latter process is called up-conversion. Up-conversion materials convert lower-energy light to higher-energy light, which is realized through excitation with multiple photons. Materials with up-converting properties are much less common than those with down-converting properties. Unlike traditional fluorescence, upconversion is so unique in nature that it makes detection of the captured target unambiguous in almost any environment, thereby providing a distinct and detectable signal for even trace amounts of material. This creates an important competitive advantage for the upconverting materials in many applications, such as clinical diagnostics, bioimaging, and photodynamic therapy, among others. There have been ongoing efforts to study and synthesize upconverting materials, especially nanoscale materials. However, most of methods reported in literatures and patents are solid/gas phase reactions, which allow less control over the size and distribution of the particles. Since the sensitivity of a detection assay using upconverting phosphors depends on the ability to distinguish between bound and unbound phosphor particles, it is preferable that the particles be of similar size and morphology. For practical implementation of phosphors as transmissive sensors, it is essential that the grain size of the phosphor be as small as practicable (typically less than about 100 nm). Very recently, we invented a method, through solution
reactions, to prepare uniform nanoparticles (below 100 nm in diameter) with upconverting properties. It allows us to have more control over the size distribution of the nanoparticles, which is a novel method for synthesizing upconverting nanoparticles. With different compositions in the starting materials, we can produce a collection of nanoparticles with several differentiable combinations of emission wavelengths. We report the preparation and modification of these nanoparticles. Key competitive features of these upconverting nanoparticles are: 1) No background interference; 2) High sensitivity; 3) Simultaneous detection of multiple analytes; 4) No fading, unknown peaks, bases, heavy metal ions, UV, X-rays, pressure, and mechanical and electrical shock; 5) Compatible with alternative testing matrices (oral fluid, whole blood, etc). Potential applications will be discussed and particularly those in biodetection will be demonstrated.

**06.21**

Supported TiO2 Nanoparticles Prepared by Reactive-Layer-Assembled Deposition Studied by XPS, STXM, STS and TPD. Zhen Song¹, Jan Hrbeck² and Richard Osgood³;
¹Applied Physics, Columbia University, New York, New York; ²Chemistry, Brookhaven National Laboratory, Upton, New York.

TiO2 is an attractive and pervaive catalytic oxide for a variety of chemical applications, particularly those involving solar energy-driven reactions. Nanoparticle forms of this oxide are of interest because they offer the possibility of size-controlled band gaps and chemical reactivity. In our work, uncapped TiO2 nanoparitcles were prepared by reactive-layer-assembled deposition (RALAD), in which Ti atoms are initially deposited on a multilayer of H2O (or NO2) grown on a Au(111) substrate at temperature <100 °C. The chemical, structural, and electronic properties of these oxide nanoparticles were studied by XPS, STXM, STS and TPD. Specifically, ~1 nm diameter TiO2 particles, formed with an H2O reactive layer, were obtained after raising the substrate temperature to 300 °C. The particles were found to preferentially aggregate around the etched surfaces of the reconstructed Au(111) surface, probably driven by the capillary force of liquid water drops that are pinned on the surfaces. Use of NO2 reactive layers yields TiO2 nanoparticles (~1 nm at 300 °C) with N2O radical ions decorating their surfaces at temperatures below 500 °C. The particle aggregates are randomly distributed on the Au surfaces at temperatures below 500 K. The particle aggregates are randomly distributed on the Au substrate. This was confirmed by the addition of NO2 with a Au herringbone structure that was left after adsorbing NO2 on it. Further annealing was shown to induce desorption of N-containing species and to leave behind flat TiO2 rutile and anatase particles (~1 nm after being annealed to 700 °K) with various single or mixed facets. More extensive annealing at 700 °K induced more rutile (100) facet nuclei. STS studies showed different electronic structure for different TiO2 particle sizes. The band gap is ~3.8 eV for the ~5 nm TiO2 particles, and it appeared larger for smaller particles. We are currently examining the chemical reponse of these nanoparticles. Thus far our TPD measurement has shown that the TiO2/Au system catalyzes the formation of formaldehyde from methanol. The nascent TiO2-particulate reactive layer is also found to be able to reduce NO to N2. This UHV compatible method for preparing well-defined TiO2 nanoparticles is ideal for molecular-level studies of reaction mechanisms of photocatalytic processes on TiO2 nanoparticle surfaces. This work is supported by Dr. Cesar A. Garcia under the contracts of DE-FG02-90ER14104 and DE-AC02-98CH10886.

**06.22**

Sacificial Bio-templates for the Formation of Nanostructured Metallic Microshells. Emma Kate Payne, Nathaniel Rosi, Can Xue and Chad Mirkin; Chemistry, Northwestern University, Evanston, Illinois.

A new material fabrication method is presented wherein diatoms, a form of unicellular algae, are used as templates for the formation of metal-coated diatoms and 3-D isobal nanosol Stratified metallic microshells. The unique characteristics of the algal nanostructured features that are inherent to the sacificial diatom template. The new materials have been characterized using scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), and the potential for these novel materials as substrates for surface enhanced Raman scattering (SERS) will be addressed.

**06.23**

Piezoelectric Properties of Solution Grown ZnO Nanocrystals. David Scrymgeour and Julia W. P. Hsu; Sandia National Laboratories, Albuquerque, New Mexico.

The drive toward smaller and more sensitive sensors for hazardous gas, explosive material, and biological agent detection is naturally leading toward the utilization of nanostructured materials and devices. The advantage of nanostructured materials is that the small size leads to enhanced surface to volume ratios ideal for ultra-sensitivity. Piezoelectric materials, already utilized in sensor applications in bulk and thin film materials, are now being grown in nanostructures. Piezoelectric nanostructures provide great utility due to their ability to directly manipulate and respond to their environments and will be used as future nanoelectronics and nanosensors. Piezoelectric zinc oxide nanocrystals are grown by solution techniques on highly textured Ag(111) films. The properties of these nanocrystals have diameters ranging from 100 nm to 2μm and lengths ranging from 100 nm to 600 nm, depending on growth time and addition of growth modifier. The large majority of the ZnO nanocrystals are oriented with their <0001> axis parallel to the substrate. By using a secondary ion mass spectrometer, in this direction for wurzite crystals, ZnO nanocrystals could grow in either the [0001] or [001] direction. The piezoelectric coefficient (d33) for these two directions have opposite sign, i.e., 180° out of phase. Using piezoelectric force microscopy (PFM), the piezoelectric response of individual ZnO nanocrystals has been characterized. PFM is able to unequivocally distinguish between (0001) and (001) oriented rods that establish crystal growth directions from the substrates. In addition, using organic growth modifiers, e.g., n-octadecanethiol molecules, the growth morphology and the physical properties of the ZnO nanocrystals can be varied. The piezoelectric response of ZnO nanocrystals grown under different conditions will be reported. The frequency dependence of the piezoelectric response will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

**06.25**


Manganese oxides are widely used as catalysts and as components in Li-Mn batteries and solid oxide fuel cells. The manganese ion can occupy the +2, +3, and +4 valence states, and a number of manganese oxide polymorphs have been identified. Synchrotron-based time-resolved X-ray diffraction (TR-XRD) was used to investigate the reduction of Mn3O4 nanoparticles with CO gas, and the re-oxidation of the resultant particles in pure oxygen. The in situ XRD data show that under a normal supply of CO, tetragonal Mn3O4 reduces to cubic MnO, and the reduction temperature is controlled by Mn3O4 nanoparticle size, as measured by XRD. As the initial Mn3O4 particle size increases, the temperation increases. The re-oxidation behavior of these particles is also dependent on the initial Mn3O4 particle size. The formation of the unstable intermediate phase Mn2O3 is observed in the oxidation of MnO → Mn3O4 → Mn2O3 when the initial Mn3O4 nanoparticles are ~25 nm. Larger initial Mn3O4 nanoparticles (45 nm) did not form Mn2O3 during oxidation. Hausmannite (Mn3O4), the most stable of the manganese oxides, is prepared by mixing aqueous solutions of manganese nitrate and ammoniumsulfonate in H2O at near room temperature. Transmission electron microscope (TEM) results show that the size of the Mn3O4 nanoparticles is controlled by varying reactant concentrations. An increase in either the HMT concentration or the Mn3O4 nitrate concentration results in a decrease in particle size. These results indicate the relationship between particle size and
reduction behavior may have significant consequences for the use of Mn3O4 nanoparticles in reducing and oxidizing conditions.

**06.26**

**Exploration of Iron Oxide Core-Shell Nanocomposites as Sensing and Catalytic Materials.** Lingyan Wang1, Jin Luo1, Xiaojing Shi2, Susan Lu2 and Chuan-Jian Zhong2,1Chemistry, State University of New York at Binghamton, Binghamton, New York; 2Systems Science and Industrial Engineering, State Univ. of New York at Binghamton, Binghamton, New York.

A key to the exploration of nanocomposites in catalysis and sensors is the development of the ability to control the size, shape, composition and interparticle spatial properties. This presentation reports findings of an investigation of the synthesis of molecularly-capped iron oxide core (iron oxide-shell) nanocomposites and their assembly towards thin film materials. Size-defined iron oxide nanoparticles were used as seeding materials for the reduction of gold precursors, which leads to the coating the iron oxide cores with gold shells (Fe oxide@Au). One unique aspect of our synthetic approach is the formation of Fe oxide@Au core-shell nanocomposites with controllable surface properties for molecularly-mediated assembly of the nanoparticles. By controlling the size of the metal cores, we can tune the capping agent properties and solution compositions, the size, shape, composition, and monodispersity can be tailored. The core-shell and thin film assembly are characterized by an array of techniques, including TEM, ED, DLS, XRD, and XPS. The as-prepared films are important for applications in biosensing and magnetic devices.

**06.27**

**Structural evolution of La1-xSrxCr1-yCoyO3 thin films for SOFCs and catalysis.** Nina Orlovskaya1, Anthony Coradito1, Christopher Johnson2 and Randall Gemmen3, 1Drexel University, Philadelphia, Pennsylvania; 2National Energy Technology Laboratory, Morgantown, West Virginia.

Nanostructured La1-xSrxCr1-yCoyO3 perovskite thin films have found important applications as a protective coating for metallic interconnect in Solid Oxide Fuel Cells or as reforming catalyst for syngas from coal. The formation of monoclinic and other basic hydrocarbon gases. The structure of La1-xSrxCr1-yCoyO3 thin films will determine the material performance and, therefore, it is extremely important to understand the mechanisms of its formation. In this research we report on the study of structural evolution of La-Sr-Cr-Co-O thin films deposited by RF magnetron sputtering on the Cr rich Fe based CROFER APU 22 alloy substrates. Three types of CROFER APU 22 substrates with different amount of impurities, such as Cr, Co, Cu, were used for the film deposition. The substrates were heated to 800°C during film deposition however the deposited film was X-ray amorphous as determined by XRD and micro-Raman spectroscopy. Upon further annealing the film transforms to the perovskite structure at 800°C. Two different mechanisms of the perovskite structure formation were discovered: the first one was a formation of perovskite phase via an intermediate LaCrO4 phase (700°C) if the annealing was done in air; the second one was a direct formation of perovskite phase without any intermediate phase if annealed in forming gas (H2/N2). The structure of the perovskite films formed by two different routes differ significantly, since the first structure formed via intermediate phase contained a significant amount of nanosize porosity, which was almost absent in case of film annealed in the reducing atmosphere of forming gas. The area specific resistance (ASR) measurements revealed a strong dependence of the substrate/film conductivity on the level of impurity, especially Si and Al that form non-conductive oxides upon oxidation. The lowest ASR equals to 0.005 ohm-cm is reported for the CROFER APU 22 alloy that has the lowest level of impurity Cr7 1.05 wt%, Al2O3 0.17 wt% and has been coated with La0.95Sr0.05Cr0.99Co0.01O3 thin film. The research results are important for design of lower temperature SOFCs as well as perovskite catalytic membrane reactors.

**06.28**

**A Non-Catalytic Silicon Nanowire Fabrication Approach and Its Device-Use Assessment.** Yung Hao, Alan Kanan Kalian and Stephen Foh, 1CNEU, Pennsylvania State University, University Park, Pennsylvania.

Polycrystalline silicon nanowires were fabricated from precursor amorphous silicon thin films by electron beam lithography resist patterning followed with reactive ion etching and solid phase crystallization. The electron beam lithography patterning determines the size, position and number of the wires fabricated. The shape of the wires could also be controlled by the reactive ion etch parameters. This technique avoids any catalyst involvement in silicon nanowire growth (e.g. vapor liquid solid synthesis), since such catalyst use may be potentially detrimental to device performance. In addition, the approach is an environmental friendly patterned-in-place technique, compared with the more common pick-and-place silicon nanowire growth processes. To convert the a-Si into polycrystalline Si, solid phase crystallization was carried out at 600 and 1000°C in a nitrogen ambient after nanowire formation. We characterized the resulting polycrystalline nanowires with Raman spectroscopy and compared them to solid phase crystallized Si films of the same thickness. The nucleation and grain growth mechanisms associated with the crystallization of our nanowires will be discussed. Electrical characterization results pertaining to nanowire device utilization will also be presented.

**06.29**

**Changes in Oligonucleotide Conformation on Nanoparticle Surfaces by Modification with Mercaptohexanol.** Sunho Park1, Katherine Alice Brown2, and Kimberly Hamond1, 1Department of Mechanical Engineering, M.I.T., Cambridge, Massachusetts; 2Biological Engineering Division, M.I.T., Cambridge, Massachusetts.

Nanoparticle labeling of DNA oligonucleotides has many applications in sensing, programmable assembly of nanostructures, and control. The linking of nanoparticles to oligos has been explored and the most common route is to use a thiol or other functional group on the 5’ or 3’ end of the oligo, leaving the bases unshocked for hybridization to its complement. However, it has been found that oligos can adsorb to gold nanoparticle surfaces through the bases on the nucleotides and then inhibit hybridization by preventing base pairing. We use chemical modification of the nanoparticle surface with 6-mercapto-1-hexanol (MCH) to control oligo conformation so that the DNA can achieve a conformation that facilitates hybridization. The Ferguson method is used to mutate the change in effective Au-DNA samples upon MCH reaction. Experimental results clearly show that the effective size increases upon the reaction with MCH, but decreases at high MCH concentrations due to different electrophoretic behaviors of the conjugate as well as the loss of surface DNA. In addition, hybridization ability of surface modified Au-DNA can be achieved by labeling the complement DNA with fluorescent molecule. By considering both effective size change and hybridization property, we can predict the real conformation of the Au-DNA conjugates at each MCH reaction condition.

**06.30**

**Nanotubes as Stationary Phase in Microfabricated Gas Concentrators and Separators.** Michael Stadtmann1, Brian Dick1, Christopher Bailey1, Ulrich Bonne2, Robert Higashi2, Alex Noy1 and Olgica Bakajin1, 1Chemistry & Materials Science, Lawrence Livermore National Laboratory, Livermore, California; 2Honeywell Laboratories, Plymouth, Minnesota.

Separation and characterization of substances has been restricted to laboratory operations in the past. Today, the instruments performing the tasks are bulky and power-hungry. In today’s world, there is an increased demand for the capability of doing rapid separation and analysis of chemical substances in the field. This requires small, portable units that consume little power, but have the separation capacity of larger desktop systems. The key to reducing dimensions and power consumption lies in microfabrication, combined with the development of novel materials that can be used for separation. This project, we are investigating the use of carbon nanotubes as a stationary phase in microfabricated gas chromatography columns and pre-concentrators. A stationary phase made of nanotubes has a significantly larger surface to volume ratio than any other stationary phase, and the increased surface area should translate to an improved separation capability. Additionally, the nanotubes are hydrophobic and show differential affinity for chemical functional groups, which makes them ideal candidates for separation of organic molecules in the presence of water. We demonstrate columns fabricated by photolithography into which the nanotubes are deposited by chemical vapor deposition. The retention and separation characteristics of these columns are evaluated and compared to other stationary phases. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48 and supported by the DARPA Micro Gas Analyzers program.

**06.31**

**Catalytic activity of nanosize amorphous iron in the process of conversion of cyclohexane.** Minasyan Varja1, Grigoryan Susanna1 and Ramik Malkhasyan1, 1Chemical Physics Institute of NAN, Yerevan, Armenia; 2Scientific production enterprise “ATOM”, Yerevan, Armenia.

Nanomaterials structured materials have wide use in catalytic processes for the
last year. These materials are obtained by different physical and chemical methods. In this paper it is presented the nanosize amorphous iron powder prepared by mechanical attrition in chemical technology. The amorphous state of iron powder is confirmed by X-ray diffraction of powders and electron microscopy. The particles of synthesized powder have size 6-10 nm. In order to form a catalyst with developed surface, Fe was put on Al2O3 (with Surfacespecific = 60 m²/g, radius of pore is 370Å and size of particle is 2 mm), preliminary heated to 400 °C. The catalytic activity of amorphous Fe and crystalline Fe is compared in the reaction of dehydrogenation and hydrogenation of cyclohexane (H2 is gas-carrier, under atmospheric pressure, and T = 250-400 °C). It is shown, that Fe has high catalytic activity and selectivity in the process of conversion of cyclohexane to benzene. The catalytic activity of amorphous nanosize Fe was also tested in the process of hydrogenation of cyclohexane in the reaction (hydrogenation of CO) within low temperature range 200-350 °C.

O6.32 Aerogel-Nanotube Composites: Growth of Carbon Nanotubes on Catalytically-Active Aerogel Monoliths Using Chemical Vapor Deposition. Stephen A. Steing 
, Mildred S. Dresselhaus 
, Jing Kong 
, Theodore F. Baumann 
 and Joe H. Satcher 
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1Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

The goal of this work is to evaluate the effectiveness of using catalyst-doped aerogels as high-surface-area substrates for growing carbon nanotubes and to study chemisorption areas (≥ 1,600 m²/g) and nanoparticulate structure of aerogels make them appealing targets for use as nanotube catalysts, as this combination of parameters offers a unique potential for high yield growth. Additionally, interaction of carbon nanotubes with their substrate could have novel applications as high-surface-area monolithic electrodes and for hydrogen storage systems. Two systems of aerogels were evaluated in this study: monolithic mixed-matrix iron oxide/alumina aerogels prepared through alkoxide-assisted sol-gel followed by evaporation of metal salts and monolithic carbon aerogels doped with transition metal (Fe, Co, and Ni) nanoparticles prepared through a metal-ion exchange technique. Nanotube growth throughout the aerogels was then induced through chemical vapor deposition of methane with hydrogen in argon at temperatures ranging from 600 °C to 650 °C. Details of the synthesis of the aerogel catalysts and derivative aerogel-nanotube composites will be discussed in terms of applications of this technique for nanotube production and in producing new, useful aerogel composites. Characterization of these materials will also be discussed.

O6.33 Characterization of Palladium Nanoparticles Using X-ray Reflectivity, EXAFS and Electron Microscopy. Yumik Sun 
, Rebecca Lasseroff 
, Cheryl Shonbrun 
, Michelle Forman 
, Anatoly I. Frenkel 
, Kwan-Tsun Kwok 
, David W. Nastasi 
 and William H. Ralovich 
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1Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York; 2Stella K Abraham High School, Hewlett, New York; 3Physics Department, University of Tokyo, Tokyo, Japan; 4National Institute of Materials Science and Engineering, K-IST, Oryong-dong, Kwangju, South Korea.

We compared the characteristics of dodecanethiolate palladium nanoparticles synthesized by two different techniques, a one-phase method and a two-phase method. From Transmission electron microscopy (TEM) we determined that the particle sizes were 4.0 nm and 2.0 nm for the 1- and 2-phase particles, respectively. Electron diffraction confirmed that their structure was FCC. The lattice constant a0 was 3.73 angstrom and 3.77 angstrom for the 1- and 2-phase particles, respectively, which were slightly shorter than 3.89 angstrom of the bulk value. The analysis with EXAFS. These data were modeled with a cuboctahedral model which implied particle sizes of less than 1.0 nm for both 1- and 2-phase particles. The discrepancy between the two techniques was attributed to Pd-S compounds which are common with this synthetic technique when the reaction does not go to completion. The dodecanethiolate Pd particles were also spread at the air/water interface. Surface pressure/area isotherms could only be obtained from particles formed in the 2-phase method which wet the water surface. X-ray reflectivity data indicated that the Langmuir monolayer was only 13 angstrom thick. TEM found the diameter of the particles in this layer was 23 angstrom; hence the particles assumed an oblate structure after spreading. A stack of 750 Langmuir monolayers were used to obtain EXAFS data. The results indicated far fewer Pd-S compounds in these samples, which may have dissolved in the water phase. The model needed to fit the EXAFS data was a monolayer of Pd particles which was 7 angstrom thick and 19 angstrom in diameter. These values were consistent with those obtained by the other methods, confirming the proposed non-spherical shape of the particles. This work was supported in part by the NSF through a grant to K-W. TF acknowledges support from the U.S. Department of Energy, Grant No. DE-FG02-03ER15477.

O6.34 Nanocrystalline Diamond as an Interface for Biomedical Applications. Zhengxing Xu 
 and Ashok Kumar 
.
1Mechanical Engineering, University of South Florida, Tampa, Florida; 2Nanomanufacturing and Nanomaterials Research Center, University of South Florida, Tampa, Florida.

Diamond is known as the material that has excellent mechanical, electrical and chemical properties. Besides these, diamond is also an ideal interface that is compatible with microelectronics and biological environments to work as an interface for biomedical systems. There are several practical benefits of using nanocrystalline rather than microcrystalline diamond thin-film, including the ability to etch a continuous film at a meter range, easier deposition of substrates with irregular geometries and the unique electrochemical behavior result from NCD films' different morphology and electronic properties compared to the microcrystalline films. In our study, nanocrystalline diamond (NCD) film was grown on Si substrate by microwave plasma enhanced chemical vapor deposition (MPECVD) system. Nitrogen gas was incorporated during the deposition to make the film conductive. Scanning electron microscopy (SEM) and Raman spectroscopy were used to characterize the film. The NCD was then treated by hydrogen plasma in the CVD chamber after the deposition to obtain hydrogen terminated surface. This hydrogenated surface is ready for bio-modification and can be used as the platform for biosensors. Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) were employed to confirm the surface hydrogenation. NCD film was utilized as a working electrode in electrochemical setup for biosensor applications. Here, we presented some preliminary results of a glucose biosensor, which was fabricated based on the functionalized NCD electrode. Carboxyl functional groups were used to functionalize the NCD electrode and to immobilize the glucose oxidase (GOX) enzyme. Cyclic voltamograms (CV) were performed to evaluate the response of the NCD electrode with different glucose concentrations. Linear calibration curve of glucose sensing has been obtained over the concentration range up to 13 mM in phosphate buffer. Dependence of temperature and sensing media affection has also been studied.

O6.35 Atomic and Electronic Structures of Pt Supported on Graphene. Kazuoyuki Okaizaki-Maeda 
, Yoshitada Morikawa 
, Shingo Tanaka 
 and Masanori Kobayama 
.
1CREST, Japan Science and Technology Agency, Kagawa, Japan; 2Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Japan; 3Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan.

Platinum (Pt) particles supported on carbon materials are used as electrocatalysts for fuel cells. We have to examine the structure and electronic state in detail to know the characteristic properties. Therefore we examined atomic structure and electronic state of Pt cluster supported on graphene, using the first-principles calculations based on the density functional theory (DFT). We calculated the Pt pseudopotentials by Vanderbilt’s ultra-soft scheme and by the norm-conserving scheme. We adopted the local density approximation in the DFT with Perdew and Wang formula (PW91) as the exchange-correlation energy functional. All the calculations were carried out using the program package STATE (Simulation Tools for Atom TEcHnology). We have treated the 1×1 cell including two carbon atoms for the adhesion of Pt(111) monolayer and the 8×8 cell including 128 carbon atoms for the adsorption of Pt(111) cluster as the calculating surface unit cell. We used the periodic slab model separated by vacuum region of about 25 Å. At first, we examined the interaction between graphene and Pt(111) monolayer. The distance between graphene and Pt(111) is 3.48 Å and the adsorptive energy is 0.09 eV/atom. The density of states (DOS) for Pt(111)/graphene system is the same with the sum of DOS’s for graphene and Pt(111) monolayer. These results show that the interaction between graphene and Pt(111) monolayer is very weak. When Pt is adsorbed on Pt(111), the Pt atom strongly interacted with the vacancy at surface. Some defect in graphene may have an important role even in the case of Pt on graphene. Next, we examined the interaction between graphene and the Pt cluster consisting of a ten atom center. It is a hexagonal bottom layer with seven atoms and a triangular top layer with three atoms. The distance between graphene and the bottom layer is about 2.7 Å. This distance is shorter than that of the adhesion of Pt(111) monolayer. This can be said that interaction between the Pt10 cluster and graphene is stronger than that between the Pt(111) monolayer and graphene. Moreover, the center atom in the hexagonal bottom layer is nearer to graphene than other atoms and that distance is about 2.5 Å. If there is a defect on graphene, the center
atom of the hexagonal bottom layer strongly interacts with that. We are planning to discuss on the electronic structure of a Pt cluster supported in detail on this day. This research was supported by the CREST, JST.

06.36
Tailoring In situ Synthesis of Metallic Nanoparticles, Encapsulated in Electropun Polymer Nanofibers. Jian-Nan Lin, Hung-Cheng Chen, Jian-Yu Chen and Changshu Kuo;
Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan.

Encapsulation of metallic nanoparticles in electropun polymer nanofibers provides a perfect solution to their durable usages in solid state sensors. The in situ nanocomposite synthesis of inorganic copper nanoparticles in one-dimensional polymer nanofibers was conducted and investigated in this research work. Block copolymers, like poly(4-vinylpyridine)-b-poly(methyl methacrylate) (P4VP-b-PMMMA), were utilized to encourage the phase separation and/or the rearrangement of hydrophilic-hydrophobic polymer segments, as well as to regulate the reduction reactions of metallic precursors in terms of the nanoparticle sizes and the embedding location. Thermal/oxidative stability and other physical properties of metallic nanoparticles encapsulated in nanofiber matrices were characterized and discussed.

06.37
Analytical TEM Observation of Gold Nano-Particles on Cerium Oxide. Tomoki Akita1, Koji Tanaka1, Masanori Kohyama1 and Masatake Haruta2; 1Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Jodai, Osaka, Japan; 2Materials Chemistry Course, Tokyo Metropolitan University, Hachioji, Tokyo, Japan.

It was reported that Au/CeO2 catalysts show high catalytic activity for low temperature water gas shift reaction and CO oxidation. Recently, it was reported that small clusters or atomically dispersed Au positively charged on a CeO2 surface were responsible for low temperature water gas shift reaction. However, the detailed structure of Au particles on CeO2 was not investigated directly. Because it is difficult to observe small Au clusters on CeO2 by conventional transmission electron microscopy (TEM) due to the disturbance of the diffraction and phase in detail by the CeO2 substrate. The structure of Au/CeO2 catalysts was observed using an analytical transmission electron microscope. Annular dark field scanning transmission electron microscopy (ADF-STEM) and energy dispersive X-ray spectroscopy (EDS) revealed that Au particles smaller than 2 nm in diameter were highly dispersed on the CeO2 support. However, the CeO2 support, which consisted of small crystals with a size of approximately 10 to 20 nm, disturbed detailed observations around the contact interface between Au and CeO2. In this work, TEM observations were performed on a model catalyst sample that was prepared using a CeO2 support with a lower surface area and poly crystalline substrate in order to study the interface structure between metal particles and CeO2. Au/CeO2 and CeO2 support were deposited on a commercially-produced, high-purity CeO2 powder using the deposition precipitation method, which is utilized for the preparation of highly dispersed Au particles on metal oxide. The Au/CeO2 model samples were also prepared by the vacuum deposition of poly crystalline CeO2 or in a poly crystalline CeO2 substrate. An FEOL JEM-3000F transmission electron microscope was used with an accelerating voltage of 300 kV. From the plane-view HRTEM observation, it was found that the patterns of moiré fringes appeared in the same direction for each Au particle, indicating that the Au particles were deposited on the CeO2 support with a preferred orientation relationship, the Au(111) plane was parallel to the CeO2(111) plane and the <110> direction of Au and CeO2 is also parallel. This orientation relationship was also observed in the profile-view TEM images. It was also found that the Au particle disappeared during observation. This change is similar to Ostwald ripening and the transport of atoms may occur by surface diffusion along the CeO2 surface. The height of the Au particle decreased layer by layer, while the length of contact interface remained unchanged, until the thickness was reduced to one atomic layer. This means that the Au atoms in the contact interface are strongly connected to the CeO2 surface. It was also observed that the Au particles were dispersed as smaller particles after irradiation by electron beam.

06.38
Colloidal-Au Replacement Assay Based on Surface Plasmon Resonance and PEGylated Gold Nanoparticles. Seiji Takeda1, Yoshitsugu Akiyama1, Yuichi Yamasaki1, Yukio Nagasaki2 and Kazuhiro Kataoka1,2; 1Materials Science and Engineering, The University of Tokyo, Tokyo, Japan; 2Research Center for Interdisciplinary Materials Science, Tsukuba University, Tsukuba, Japan; 3Center for Disease Biology and Integrative Medicine, The University of Tokyo, Tokyo, Japan.

A novel approach to highly sensitive quantification of low molecular weight (LMW) compound was studied here based on a combination of functionally PEGylated gold nanoparticles with surface plasmon resonance (SPR). Gold nanoparticles (diameter ∼ 20 nm) functionalized with lactosyl-pol(ethylene glycol) (PEG) disulfide dimer revealed a remarkably larger shift in plasmon angle through the binding into Ricinus communis-insensitive (RCA120)-inspiring sensorchip than free lactosyl-PEG. Furthermore, the plasmon shift due to the gold nanoparticles binding considerably increased with decreasing of a thickness of dextran layer on the SPR sensorchip because of the increased coupling effects of localized surface plasmons on the gold nanoparticles and propagating surface plasmons on the substrate gold. Injection of free D-galactose into RCA120-immobilized sensorchip with pre-adsorbed lactosyl-PEGylated gold nanoparticles yielded the elution of the nanoparticles in the manner proportional to galactose concentration (0.1-50 ppm), revealing the substantial change in the plasmon angle. This method of D-galactose sensing through the surface plasmon elution of pre-adsorbed particle from the sensorchip surface would be applicable for highly sensitive SPR quantification of various LMW analytes, which are known to be difficult to detect by the conventional SPR sensing regime.

06.39
pH Sensor Application of Oxide Nanomaterials. Chi-Chung Yu and Jih-Jen Wu; Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan.

Highly oriented ZnO, TiO2 and Fe2O3 nanorods, which are grown on Si substrates using a simple catalyst-free MOCVD method, have been employed to be the sensing membrane in an extended gate field effect transistor for the measurement of pH of the solutions. The ZnO, Fe2O3, and TiO2 nanorods are 44.8, 25.4, and 55.5 and 57.6 mV/pH, respectively, in the range from pH3 to pH11. The enhancement of the pH sensibility of the ZnO and TiO2 nanorods in comparing with the corresponding thin films is observed. In contrast, the iron oxide nanofilms possess superior pH sensing properties with a sensitivity of 74.2 mV/pH, which is much higher than the maximum limiting value of the Nernst response according to site-binding model. The possible mechanism for the pH sensing properties of the oxide nanostructures will be discussed in this paper.

06.40
Nanowire for Detection of Biological Species. Kyung Ah Jeon1, Jong Hoon Kim1, K. H. Yoo2, Hyo Il Jung3 and Sang Yeol Lee1; 1Electrical and Electronic Engineering, Yonsei University, Seoul, South Korea; 2Department of Physics, Yonsei University, Seoul, South Korea; 3School of Mechanical Engineering, Yonsei University, Seoul, South Korea.

Si nanowires (NWs) were fabricated by a Nd:YAG pulsed laser with the wavelength of 355 nm without catalysts metal. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images indicate that the products are crystalline silicon NWs, which is a robust chemical sensitivity of nanowire. A highly sensitive and robust chemoresistive thin film nanowire were used to detect DNA down to at least a picomolar concentration range. The electrical properties of NWs are investigated as a function of DNA sequence length. The silicon NWs for sensitive, label-free, real time detection of a wide range of biological species could be explored in vivo diagnostics.

06.41
Microstructure and Electrical Characteristics of Plasma Sprayed Thick Film Mn-Co-Ni Oxide Thermistor. Shanshan Liang, B. G. Ravi, S. Sampath and R. J. Gambino; Center for Thermal Spray Research, Department of Materials Science and Engineering, State University of New York, Stony Brook, Stony Brook, New York.

Mn-Co-Ni-O spinel, owing to its large temperature dependent resistivity, is an attractive ternary system for negative temperature dependent (NTC) thermistor applications. Structural and electrical characteristics are presented for thick film Mni.56Co0.9Ni0.48O4 thermistor produced by thermal spraying. The composition of Mn-Co-Ni-O spinel, owing to its large temperature dependent resistivity, is an attractive ternary system for negative temperature dependent (NTC) thermistor applications. Structural and electrical characteristics are presented for thick film Mn1.56Co0.9Ni0.48O4 thermistor produced by thermal spraying. The composition of Mn1.56Co0.9Ni0.48O4 is of particular importance because it is very near the resistivity minimum for the ternary oxide. A citrate-nitrate gel combustion technique was employed to synthesize nanostuctured powders which were used as feedstock in plasma spraying. Phase evolution coupled with microstructural analysis as a function of post deposition heat treatment temperature indicate thermal spraying of spinel powders resulted into nanostructured coatings with rock salt
structure which later transformed to cubic spinel after a post heat treatment at 600 oC/3h. The electrical resistivity of the coatings was measured using four-probe method in the temperature range of 20 oC to 210 oC. The electrical resistivity and activation energy show strong dependence on crystalline phase and microstructure of the coatings. The resistivity of coating heat treated at 600 oC/3h varies from 41.2% ohm-s/cm to 65 ohm-cm (207 oC) with an activation energy of 0.278 eV. For the coating heat treated at 700 oC/3h, the resistivity varies from 7887 ohm-cm (33 oC) to 121 ohm-cm (207 oC) and has an activation energy of 0.287 eV. To estimate the thermistor constant B, the resistivity value was calculated as R(T)=R0*exp(B/T), where R0 is the resistance when the temperature approaches infinity. The estimated B for samples heat treated at 600 oC/3h and 700 oC/3h were 3225K and 3353K, respectively. The in-spray sample, which has the rock salt structure, shows a slightly complex temperature-dependence resistivity which begins to decrease on heating above 50 oC probably due to the change in valence state of cobalt. The TCR, the temperature coefficient of resistance, for samples heat treated at 33% -42%, in the temperature range from 20 oC to 200 oC, which is in good agreement with reported values [1]. Reference: [1] Hideo Aoyama, in High-Film Sensors, M. Fraden, ed., Elsevier Science B.V. 1994, p 127. Acknowledgment: This work is supported by the USAF program of AFOSR. Award #DBMR-0080021.

SESSION 07: Biosensors II
Chairs: Nicholas Kotov and Chuan-Jian Zhong
Wednesday Morning, November 30, 2005
Room 200 (Hynes)

8:15 AM *07.1
AuFe alloy nanoparticles for biological applications,
Katherine Alice Brown
1Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

We report the synthesis of water soluble, monodisperse AuFe alloy nanoparticles ranging in diameter from 7 to 14nm. Synthesis involves simultaneous reduction of Fe3+ and Au3+ in water to yield alloy nanoparticles. Bulk studies of AuFe alloys have shown interesting magnetic and optical properties but previously nano-sized alloy synthesis techniques have been limited to electron beam methods, resulting in particles of limited solubility. Solution phase synthesis allows for more versatile particles. The elemental content of Fe varies from 1%-3% and can be increased by decreasing the relative amount of reducing agents. Nanoparticles exhibit ferromagnetic behavior as measured by SQUID, and magnetic properties vary with Fe content. Spin glass behavior is observed in the higher Fe content samples. The AuFe Nanoparticles also exhibit a surface plasmon peak similar to that of plain Au nanoparticles, which redshifts with higher Fe content. These particles can be easily conjugated to thiolated DNA, as evidenced by gel electrophoresis.

8:30 AM *07.2

The drive for early disease detection, the growing threat of bioterrorism, and a vast range of challenges more generally in biotechnology has markedly amplified the demand for ultrasensitive, high-speed diagnostic tests. This presentation describes efforts to develop platforms and readout methodologies that potentially address demands in this arena through a coupling of nanometric labeling with surface enhanced Raman spectroscopy, and micromagnetic and scanning probe microscopic readout concepts. Strategies will be described for both the fabrication and read-out of chip-scale platforms that can be used with each novel readout modality. Examples will focus on the use of protein arrays as platforms targeted for immunoassays in early disease diagnosis and the rapid, ultra-low level detection of cancer markers and viral pathogens. Each example will also discuss challenges related to sensitivity and nonspecific adsorption and to fluid manipulation at micrometer length scales.

9:00 AM *07.3
Carbon nanotube biosensors with DNA aptamers as molecular recognition elements, Jeong-O Lee1, Hye-Mi Suh1, Kooheon Won1, Yong Hwan Kim1, Byung Hwan Ryu1, Pil Sun Na2, and Byungkyu Kim; 1Advanced Tech. Div., Korea Research Institute of Chemical Technology, Daejeon, South Korea; 2Department of materials engineering, Chungnam National Univ., Daejeon, South Korea; 3Department of physics, Chonbuk National Univ., Chonju, South Korea.

We report the real-time detection of protein using SWNT-FET based biosensors comprising DNA aptamers as molecular recognition elements. Anti-thrombin aptamers that are highly specific to protein thrombin were immobilized on the sidewall of an SWNT-FET using C18-Twee linker molecules. The binding of thrombin aptamers to SWNT-FETs causes a rightward shift of the threshold gate voltages, presumably due to the negatively charged backbone of the DNA aptamers. Upon addition of thrombin to the thrombin aptamer functionalized SWNT-FETs of different configurations, the electron flow was observed, thereby demonstrating the possibility realizing highly selective nanotube-based biosensors.

9:15 AM *07.4
Large-scale, label-free, parallel electrical detection of proteins, nucleic acids and viruses by high-throughput ultrasonic nanowire FET arrays, Guo Peng Zhou1, Fernando Pobletsky1, and Charles M. Lieber1; 1Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; 2Division of Engineering and Applied Science, Harvard University, Cambridge, Massaachusetts.

Large-scale, label-free, real-time, parallel electrical detection of proteins, nucleic acids and viruses are demonstrated by silicon nanowire field-effect transistor arrays. Composed of hundreds of individually electrically addressable nanowire devices with highly sensitive and reproducible performances, these nanowire arrays can be controllably modified by solution arrays of antibodies or cell-surface receptors with precise device registration, and show discrete conductance changes characteristic of highly selective binding and unbinding of a variety of target biomolecules, thus providing a general and powerful platform for high-throughput real-time parallel detection and rapid screening of libraries of biomolecules. Studies show that proteins, nucleic acids and viruses can be routinely detected at femtomolar concentrations with high selectivity even in undiluted serum samples, and that simultaneous incorporation of control nanowires in a single array enables discrimination against false positive/negative signals. Ten of proteins have been detected in parallel with femtomolar sensitivity, and multiple viruses have also been simultaneously and selectively detected at the single virus level. In addition, nucleic acid receptors were used for real-time telomerase binding activity and small molecule inhibition assays that could be carried out using the unamplified extracts from as few as 10 tumor cells. The integrated nanowire sensor arrays open up substantial opportunities for diagnosis and treatment of complex diseases such as cancer, detection of biological threats, and fundamental proteomic and biophysical studies.

9:30 AM *07.5
Complementary Detection of Prostate-Specific Antigen Using Indium Oxide Nanowires and Carbon Nanotubes, Marco Carrelli1, Chao Li3, Henry Lin4, Mark E. Thompson1,2, Fumiki Ishikawa2, Ram Datar3, Richard Cote4 and Chongwu Zhai1,2; 1Chemistry, University of Southern California, Los Angeles, California; 2Material Science, University of Southern California, Los Angeles, California; 3Electrical Engineering/Electro-physics, University of Southern California, Los Angeles, California; 4Pathology, University of Southern California, Los Angeles, California.

Functional sensing devices for the complementary detection of prostate-specific antigen (PSA) have been fabricated using n-type indium oxide nanowires and p-type carbon nanotubes. PSA is an oncological marker for the presence of prostate cancer. Despite its high importance, detection of PSA using nanowires or carbon nanotubes has never been reported. Two key innovations have been made with respect to previously fabricated nanosensors. First of all, a novel approach has been developed to covalently attach antibodies to indium oxide nanowire surfaces via the onite surface synthesis of a succinimidyl linking molecule. Secondly, a combination of indium oxide nanowires and carbon nanotubes based devices was used for the detection of PSA, which revealed complementary electrical response upon PSA binding. The electrical properties of the devices were measured in both dry and fluidic condition. In a dry environment, the threshold voltage on the nanowire devices shifted of +6 V whereas that of nanotube devices shifted of -3 V (complementary response). In fluidic environment, we tested the specificity of our devices by trying to detect a non-target protein, which resulted in a "no response". When PSA was present in the fluidic solution, we observed a 1.3% increase in the conductivity of the nanowire device (PSA level: 0.14 nm) while the conductivity went down of 2% when nanotubes devices were used (PSA level: 1.4 nm). This work demonstrated effective detection of PSA in solution as low as 5 ng/mL, a level useful for clinical diagnosis of prostate cancer.

10:15 AM *07.6
Characterization of Novel Glucose-Sensitive
Novel Glucose-sensitive Nanogel particles based on Poly(N-isopropylacrylamide) were prepared by precipitation polymerization in aqueous phase. Laser Light Scattering was used to characterize the volume phase transitions of a series of nanogels in response to the variation of glucose concentration and temperature. We have found that the nanogel particles swell enormously and rapidly with an increase in glucose concentrations at room temperature. More importantly, the nanogel can undergo a reversible temperature-sensitive swelling and collapsing process to release glucose. Based on these special properties, the nanogels could be potential candidates for glucose sensing applications. The glucose sensitivity of the size of the nanogels could be controlled through the ionic strength as well as the amount of functional groups in the polymer network chains.

10:30 AM 3Q.7
Plasmonic Nanostructures for SERS sensing: comparing geometries and local field properties. 
Nagami Halas1,2,3, Chris Oubre4,5, Peter Nordlander1,2,3, Hui Wang1,2,3, Joseph Jackson1,2,3, Nate Grady1,2, Felicia Tam1,2, Thomas Huser4,5, Chad Talley4,5, Chris Hollars4,5, Stephen Lane1,2, Carly Levin4,5, and Muhammed Gheith1,2,3. 1Department of Electrical and Computer Engineering, Rice University, Houston, TX; 2Department of Physics and Astronomy, Rice University, Houston, TX; 3Department of Chemistry, Rice University, Houston, TX; 4Chemical and Materials Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California; 5Physics and Advanced Technologies Directorate, Lawrence Livermore National Laboratory, Livermore, California; 5NSF Center for Biophotonics Science and Technology, University of California, Davis, Sacramento, CA; 6Laboratory for Nanophotonics, Rice University, Houston, Texas.

Our ability to design and fabricate high sensitivity nanosensors based on local electromagnetic field driven processes such as enhanced Raman scattering (SERS) depends on our abilities to correlate the SERS intensities from individual nanostructure substrates with electromagnetic properties calculated specifically for each geometry we prepare. We used Finite-Difference Time-Domain (FDTD) simulations to calculate the electromagnetic SERS intensities from nonresonant molecules bound to individual nanospheres, nanoshells and nanosphere and nanoshell dimers and compare the measured intensities with theory. Electromagnetic analysis of the near field properties for these structures was performed using Mie and FDTD methods. Strong qualitative correlations between experimental SERS intensities and local field values were obtained for these substrates. In addition, the effect of local nanoscale roughness was addressed both experimentally and theoretically.

11:00 AM 3Q.8
Urease-composite Nanofibers as Urea Biosensing Material. 
Katarzyna Maciejewska-Gonnella, Peter Petashkoff, Materials Science and Engineering, Stony Brook University, Stony Brook, New York.

As the human body digests amino acids it generates a byproduct known as urea. Urea is filtered out of the blood stream and excreted through the kidneys, and the rest gets emitted through the gastrointestial tract and skin. Elevated urea readings detected in human blood or urine can be a warning signal of various ailments ranging from dehydration to renal failure. Majority of urease biosensors currently available utilize urease (urea amidohydrolase) E.C. 3.5.1.5. The irreversible reaction based biosensor where the analyte undergoes a chemical exchange catalyzed by the selective receptor and therefore gets consumed in the process, produces a measurable substance used indirectly to determine the analyte concentration. Urease catalyzes hydrolysis of urea according to reactions in Figure 1, and the rate of reaction is 1014 times greater when the enzyme is present. Urea H2N-CO-NH2 → NH2 + H2N-CO-NH2 → NH3 + H2O → H2N-CO-OH H2O → H2N-CO-OH H2O → NH3 + H2O3 → NH2 + H2O3 + H+ + OH- Figure 1. Hydrolysis of Urea Urease has been immobilized by methods of entrapment, microencapsulation, covalent attachment, and adsorption. This study unveils electrospinning as a novel enzyme immobilization technique. Composite nanofibers of urease in 80% phosphate buffered saline and polyvinylpyrolidone (PVP) were prepared by the electrospinning technique. Reactivity measurements for urease/polyamide nanofibers were recorded for differently concentrated urea solutions by measuring the ammonia concentration generated in the reaction using the Thermo Orion Ammonia Electrode. Analysis of the morphology of electrospun urease/polyamide nanofibers was performed by Scanning Electron Microscopy. The nonwoven mats collected offer a high surface area to volume ratio, essential to a fast response time and surface reactivity. The material studied advances over prior technology with faster response time, increased sensitivity range, a more versatile design, and improved storage stability.

11:15 AM 3Q.9

Vertically aligned carbon nanofibers are a unique class of carbon-based materials that promise powerful tools for biological detection. Previous work has shown that materials composed of carbon have superior stability in biological media in comparison to other commonly used substrates for biological detection (e.g., gold, silicon, and graphene). Additionally, the nanometer range of each vertically aligned carbon nanofiber (60-80 nm) allows the opportunity for high density electrode arrays as well as increased sensitivity to low analyte concentrations. The ability to control the length, density, and locations of nanofibers enables us to grow carbon nanofiber forests of densely packed sensing elements or individual electrically isolated nanofibers on electrodes. This flexibility affords fabrication of nanofiber electrode structures optimized for diverse applications. We have developed both a photochemical and an electrochemical method for functionalizing these materials with biological molecules as a first step in using nanofiber electrodes as biological recognition elements in electrochemical detection. We used the photochemical method to terminate nanofiber forest electrodes with amines, which are a versatile starting point for covalently linking oligonucleotides and proteins to the surfaces. We determined, using fluorescence and colorimetric techniques, that these biologically modified nanofiber electrodes are biologically active, selective, and stable. Additionally, we found that much of the nanofiber sidewalls were functionalized and biologically accessible - using fluorimetry we determined that the absolute number of DNA molecules hybridized to complementary-DNA-functionalized nanofiber electrodes was 2.3 x 10^14 molecules per cm^2. This value was ~8 times higher than the density of DNA molecules hybridized to flat glassy carbon electrodes and implies that the nanofiber forest geometry somehow may have greater surface area. This chemistry is also used to link horseradish peroxidase to the nanofiber electrodes, and the resulting immobilized enzymes were determined to be active and could be detected electrochemically using no chemical mediators.

Additionally, we have developed an electrochemical functionalization method which allows for electrically-addressable biomolecular functionalization of patterned nanofibers. This method has enabled us to discretely functionalize individual sub-micron nanofiber regions with different DNA sequences on the same chip using no microfluidics, and will be useful for multiplex detection on a single chip.

11:30 AM 3Q.10
Genetic Control of Nanoparticle Assembly in Response to Chemical Stimuli Using DNAzymes and its Application as Colorimetric Sensors for a Broad Range of Analytes. Yi Liu and Juewen Liu; Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois.

Genetic control of synthesis and properties of nanomaterials in response to chemical stimuli under conditions and protocols is one of the hallmarks in biology. Employing such a process in nanoscale science and engineering can result in novel nanomaterials that rival or even go beyond the structural and functional properties of naturally occurring materials. Toward this goal, we have taken advantage of recent advances in biology where catalytic DNA molecules (DNAzymes) can be selected from a large (up to 1015 different molecules) DNA library with specific binding selectivity toward an analyze of choice, and high catalytic activity such as cleavage [1,2]. By using DNAzyme for directed assembly gold nanoparticles, genetic control of such assembly in response to chemical stimuli as metal ions [3] or organic molecules [4] have been demonstrated. Because of the highly intense color change from the blue assembled nanoparticles to the dispersed red particles, this work has resulted in simple, sensitive and selective colorimetric sensors for a number of molecules [5,6]. A careful investigation of the DNAzyme biology [7] has led to a new derivative of DNAzyme that allows a tunable assembly of nanoparticle and thus tunable dynamic range of assembly [3]. In addition, a detailed understanding of DNAzyme and nanoparticle interactions resulted in substantial shortening of detection time from about 2 hours to 10 minutes and from 50 oC heating to ambient temperature operation [8]. In addition to controlled assembly of materials in response to chemical stimuli, biology also controls the disassembly of materials in response to chemical stimuli so that useful materials can be released and complex processes can be prevented. We have recently succeeded in employing such a process in disassemble gold nanoparticle aggregates in response to metal ions such as Pb2+. This endeavor has resulted in even further improvement of the colorimetric signal by using a light-down sensor into a light-up sensor. Light-up sensor is preferred

11:45 AM Q7.11 Understanding Surface Biosensor Liquid Crystal Textures. Benjamin Wincure and Alejandro R. Rey; Chemical Engineering, McGill University, Montreal, Quebec, Canada.

In the past, many studies reported on specific surface treatments that caused nematic liquid crystals to orient along a particular direction. Research is now focusing on the methodical quantitative disruption of these special surfaces, in the search for new sensor devices, such as biosensors where the addition of proteins and/or viruses to the surface cause liquid crystal textures with deformations and defects. These sensors work by visualizing the nematic liquid crystal deformations and defects using conventional polarization microscopy and then quantifying this texture in terms of a polarized light intensity, which is correlated to the amount of protein or virus. To date, a quantitative characterization of the disrupted surfaces has not yet been achieved, but the bounding surfaces should contain an unknown distribution of disrupted nematicropic regions, and their proportion to the texture, its operation and success, surprisingly little is known about the exact nature of the nematic liquid crystal textures generated in these surface sensor devices. The Time Dependent Ginzberg - Landau (TDGL) model with an order parameter was used together with the Landau - de Gennes equation to better understand the formation of non-uniform, defect-containing nematic liquid crystal textures near decorated solid surfaces. The model predicts two director easy axes at the isotropic-nematic interface normal and tangential to the interface. Based on simulation results, surface anchoring, interface shape, and the angle between the interface and surface determine which defects and deformations will form in the nematic phase. The two opposite front easily axes tend to crease defects and create a splay/ twist/bend deformations as follows: (i) When the curvature of the isotropic-nematic front brings together interface directors with opposing easy axes, and (ii) As the isotropic-nematic front travels past a switch in the solid surface anchoring.

SESSION O8: Chemical Sensor II

Chairs: Nicholas Kotov and Catherine Murphy

Wednesday Afternoon, November 30, 2005

Room 200 (Hynes)

1:30 PM O8.1 Molecular Spring Assemblies of Nanoparticles and Nanowires. Nicholas A. Kotov1, Jaebeom Lee1 and Alexander Govorov2; 1Chemical Engineering, University of Michigan, Ann Arbor, Michigan; 2Physics, Ohio University, Athens, Michigan.

The development of micro- and nanofluidics devices demands in-situ measurements of many parameters in the stream of liquids. Local gradients of solvent concentration, temperature, pH and other parameters have tremendous importance for the development of lab-on-a-chip applications and similar analytical tools. The same problem also appears in biomedical fields that require evaluation of local concentration or intricate generation of 3D cell scaffolds, which affect the development of cells residing on the scaffolds. Both tasks are difficult to accomplish using traditional sensor deployment schemes, which often require substrate and wires. In this project, we address these problems by designating a nanoscale sensing device from different types of nanoparticles and nanowires connected by molecular springs made from flexible PEG oligomers. A library of assemblies of nanoparticles and nanowires was created using PEG tethers. The polymeric linkers afford continuous and dynamic change of conformations in such structures leading to the variations of the distance between the nanoscale colloids reversibly changes depending on conditions or analyte concentration and can be evaluated by fluorescence measurements. Plasmonic-exciton interactions result in tremendous enhancement of luminescence and for some systems in characteristic wavelength shift depending on the analyte concentration. Understanding plasmonic-exciton interactions will contribute to the photonic and nanoelectronics and create a knowledge base for other technologies such as lasing in nanomaterials, energy conversion, and nanoscale electronics.

1:45 PM Q8.2 Metal Nanoparticles for Optical Sensing, and Metal Oxide Nanoparticles for Catalysis. Catherine J. Murphy; Dept. of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina.

Gold and silver nanoparticles of various shapes have been made by a seed-mediated growth approach in water and in air. Nanowires, nanorods, nanocubes, etc. have been prepared in high yield, and all these different shapes have correspondingly different optical properties. We compare different shapes of nanoparticles, for their abilities as surface-enhanced Raman scattering substrates, and for their capabilities in darkfield optical microscopy imaging. We also show preliminary data on lanthanum-copper-oxide nanorods in which these oxide nanorods are catalysts for hydroxylation of phenol.

2:15 PM Q8.3 Surface Enhanced Raman Scattering on Physically Self-assembled Ag Nanorod Arrays. Motomizu Suzuki1, Yohsini Wada1, Kaoru Nakajima1, Konji Kimura2, Takao Fukuda1,2 and Yasuhige Mori3; 1Department of Micro Engineering, Kyoto University, Kyoto, Kyoto, Japan; 2Kyoto CREATE, JST, Seika, Kyoto, Japan; 3Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto, Japan.

For applications of local plasmons in noble metal nanoparticles to chemical/biological sensors, it is important to control the shape and arrangement of the nanoparticles. Recently, we have demonstrated the direct formation of Ag nanorods with a quasi-square major axis on a template layer of SiO2 having a strongly anisotropic surface morphology. [1] In this surface-enhanced Raman scattering (SERS) of these Ag nanorod arrays. Template layers of SiO2 with anisotropic surface morphology were prepared by the bideposition technique on a glass substrate in our dynamic oblique deposition (DOOD) apparatus bideposition. During the bideposition, the deposition angle measured from the surface normal, was fixed at an angle of 82°, while the azimuthal angle was changed rapidly by 180° with each deposition of a 10-nm-thick layer. After repeating 15 cycles of the bideposition, Ag was evaporated at a deposition angle of 70° onto the fabricated template layer. The amount of deposited Ag was 5-10 nm in average thickness, which was so minute that the Ag layers remained discontinuous on the template. Owing to the shadowing, the major axis of the Ag nanorods was formed perpendicular to the deposition plane of SiO2. The Raman spectra were measured for the nanorod arrays immersed in the aqueous solution of 4,4′-bipyridine (bpy) using the excitation laser of a wavelength of 785 nm. The spectra characteristic for the SERS of 4,4′-bpy were observed for the solution of the concentration down to 1 μM. The intensity of the SERS peaks depended strongly on the polarization of the excitation light. In addition, the nanorod arrays exhibit strong anisotropic optical absorption. These properties can be understood in terms the plasma resonance that is sensitive to the shape of the nanorods. [1] M. Suzuki, W. Maekita, K. Kishimoto, S. Teramura, K. Nakajima, K. Kimura and Yasunori Taga, Jpn. J. Appl. Phys., 44 (2005) L116.

3:30 PM O8.4 Electrochemistry of Magnetostrictive Nanosensor Array. SongXing Li, Lisa Orona and Z.-Y. Cheng; Materials Research and Education Center, Auburn University, Auburn, Alabama.

A novel type of nanosensors based on magnetostrictive bars is induced. The sensitivity of the nanosensor is simulated. The results show the high performance of this nanosensor, which is capable to detect a single bacterium or even a few viruses. The fabrication of the nanosensor is reported. The magnetostrictive material used in the research is iron-iron amorphous alloy. The experimental data indicate that this alloy is a good candidate for developing the nanosensor. The morphologies and structure of the nanoarrays with diameters of 50, 100, and 200 nm are reported.

3:45 PM Q8.5 Single-Walled Carbon Nanotube Networks for Sensor Applications. Elena Belyakova, Mikhail E. Iksis and Robert C. Haddon; University of California, Riverside, California.

We present the results of a study on the development of advanced chemical sensors based on single-walled carbon nanotube (SWNT) networks. The SWNT networks provide an attractive electronic configuration because they are easy to fabricate and give reproducible characteristics. The study demonstrates the role that chemical modification of SWNTs plays in the sensor performance. The chemistry of SWNTs provides tremendous opportunities to tune the sensitivity and selectivity of SWNTs in detecting low concentration of gas molecules with high accuracy. We will discuss the response of the electronic properties of functionalized SWNTs to various gas analytes and provide some insight into the mechanism of detection. We will
4:15 PM Q8.6

Nanoparticle SnO2 films as gas sensitive membranes. Benedikt Schumacher1,2, Dorothee Vinga Szabo2, Sabine Schlabach2, Rolf Oechs1, Harald Müller1 and Michael Bruns2; 1Institute for Microsystem Technology (IMTEK), Albert-Ludwigs-University, Freiburg, Germany; 2Institute of Materials Research III (IMF III), Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany; 3Institute for Instrumental Analytics (IFIA), Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany.

Tin dioxide, a wide-band gap n-type semiconductor oxide is commonly used as gas sensing material. In the case of the Karlsruhe Micro Sensor the central gas-sensitive microarray is based on a sputtered SnO2 film. The electrical conductivity is highly sensitive to the composition of the ambient atmosphere and is measured between adjacent parallel platinum strip electrodes. At present the microarray consists of 38 sensor elements on an area of 4x8mm2. Due to their high surface-volume ratio, nanoparticles are very promising for the improvement of the sensor performance. However, spin-coating deposition using colloidal solutions of nanoparticles poses the problem of particle growth, as the operation temperature is in the range of 575K and higher. Therefore one expects strong improvements in thermal stability by applying coated nanoparticles, e.g. SnO2/SiO2 nanocomposites. It is known that such a coating reduces the sintering activity of the kernel. Thus in a new approach gas sensitive nanoparticles are produced by the Karlsruhe Microwave Plasma Process and deposited in-situ on a substrate, already equipped with the electrode array. The microwave plasma process is versatile and well suited for the synthesis of coated nanoparticles. The proof of concept shows, that mechanically stable, nanoscaled and nanoporous gas sensing layers can be deposited. In this study in a first step synthesis and deposition parameters of SnO2 were elaborated, and sensitivity tests performed. The morphology and structure of nanoparticles was characterized by X-ray diffraction and TEM-methods, the layers by SEM techniques and by XPS. The sensitivity of the nanogranular layer was determined in comparison with a standard microarray. As precursor, SnCl4 was used; Ar with 20vol.% O2 was used as reaction gas. Particles crystallized in the tetragonal cassiterite structure. It was found that a feeding rate of 6.1ml/h leads to particles with crystallite size in the region of 2nm, whereas feeding rates of 20ml/h result in approximately 6nm particles. With the low feeding rate columnar porous layers of 200nm thickness were obtained after 1min deposition time. This thickness is comparable to the one of sputtered layers. The lower the feeding rate, the less residual chlorine, stemming from the precursor, is detected in the powders and layers. It disappeared while heating the layer at 575K for 3 days. The fabricated sensors showed 10 times higher sensitivity to isopropanol, compared to the standard array. The time of response was equivalent to the standard step. The development of SnO2 nanocomposites was the lack of direct experimental measurements of the assembly process. This paper describes a study of the kinetic and thermodynamic properties for the mediator-assembly of gold nanoparticles in solution based on photometric measurements of surface plasmon (SP) resonance bands. Gold nanoparticle cores (~5 nm) encapsulated with tetraoctylammonium bromide shells were studied as a model system. The nanoparticles were assembled into 3D spherical assemblies via the mediator-template assembly which is based on a multidentate ligand (e.g., (MeSi(1H2SMe3)) functions as a mediator whereas the tetraoctylammonium salt molecules function as template agents. The temperature dependence of the SP band in the mediator-template assembly provides important information about the kinetic and thermodynamic parameters such as the reaction rate constant and the reaction enthalpy are obtained. An important conclusion is that the mediator-template assembly of nanoparticles is driven by enthalpy change in which the van der Waals interaction of the templating molecules plays an important role. Implications of our findings to the exploitation of the unique interparticle interactions for sensing applications will also be discussed.

4:45 PM Q8.8


We have shown that single-walled carbon nanotube field effect transistors (swCN-FETs) functionalized with single-stranded DNA (ss-DNA) have many desirable attributes as chemical sensors. In these devices, ss-DNA acts as the chemical recognition site, and the swCN-FET as the electronic readout component. SwCN-FETs functionalized with ss-DNA respond to gas phase analytes that do not cause a detectable current change in bare swCN-FETs. The sign and magnitude of the current change in the device depends on the type of analyte being sensed and the precise DNA sequence. Ss-DNA/swCN-FET sensors detect a variety of chemical vapors with response and recovery times on the scale of seconds. The sensor response is reproducible for at least 50 air-analYTE cycles, suggesting that it is stable, and long-lasting. Ongoing work to optimize the electron channel in the nanotube is expected to demonstrate the possibility for the creation of a large library of nanoscale sensors based on the specific interactions between designed nucleic acid biopolymers and their target chemicals and biomolecules. This could lead to applications in disease diagnosis and homeland security.

SESSION O6: Poster Session: Nanoparticles and Nanostructures in Sensors and Catalysis III

Chair: Wayne Daniell, Chuan-Jian Zhong and Shuqin Zhou

Wednesday Evening, November 30, 2005

8:00 PM

Exhibition Hall D (Hyne)

O9.1 Functionalized Y-junction singlewall carbon nanotube mats for carbon monoxide sensing applications. Harindra Vedala, Somenath Roy, Jun Huang and Womong Choi; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

Polyaniline (PANI) modified Y-junction single wall carbon nanotube mats (SWNTM) are used for the detection of carbon monoxide (CO) gas in air. Carbon monoxide on inhalation results in formation of carboxyhemoglobin in human body thereby leading to fatality at high concentrations. Though there exists several commercially available carbon monoxide sensors majority of which are based on electrochemical techniques, lack the ease of fabrication and high sensitivity. Carbon nanotubes with their excellent electrical properties and large specific surface area are shown to have high sensitivity for various gases like ammonia. Although these Y-junction SWNTM are of great interest for gas detection due to their heterogeneous geometry resulting in semiconducting behavior. To enhance the sensitivity, platinum and tin nanoparticles are incorporated into the PANI matrix by electrochemical deposition from an aqueous solution containing K2PtCl6 and SnCl4.5H2O. Carbon monoxide is detected from the increase in conductivity of the functionalized Y-junction SWNTM on a substrate with interdigitated electrodes. The cross sensitivity for environmental changes such as humidity effect on the sensor is also investigated by selectively functionalizing the nanotubes with polyvinyl alcohol.


Carbon nanotube (indigenously grown using chemical vapor deposition technique) based working electrode is fabricated on silicon substrate for detection of total cholesterol in serum. Immobilization of 2',2'-diaminobenzaldehyde reagent (a carbonyl chromophore) is done by entrapment of the enzyme in a bio-inspired, water insoluble polymer, polyvinyl alcohol (PVA), which also increases the hydrophilicity of the carbon nanotube surface (with experimental evidence) and thereby facilitate the intimate attachment of the protein molecules. For superior heterogeneous electron transfer, a redox mediator, potassium ferrocyanide is added.
to the enzyme solution. Also, addition of trehalose offers better enzyme stability for successive operation. Cyclic voltammetry also shows that the creation of cholesteryl isomer C/t, which covers the entire range of possible cholesteryl concentration in human blood. Horseradish peroxidase (HRP) is coin mobilized on the working electrode and the influence of relative concentrations of the enzyme on the sensitivity is studied. Because of the insolubility of the lipid in aqueous medium, a surfactant ( Triton X-100) is used in the test solution and its concentration effect is investigated on the sensitivity. The influence of interferences, like glucose, ascorbic acid and uric acid on the pH, is also studied. The physicochemical properties of the NFO are also determined. Owing to its compatibility with standard silicon microfabrication technology, the signal processing circuitry can also be integrated onto the same silicon substrate yielding a compact miniaturized biochip for clinical applications.

O9.3 Position Controlled Growth in Carbon Nanotubes Catalyzed by an Iron Nanodot Array. Jun-ichi Fujita1,2, Takahito Mukawa1,4, Satoshi Okada1,4, Ryota Kobayashi1,4, Masahiko Ishida2,4, Takeshi Ichihashi2,4, Yukinori Ochiai2,4 and Shinji Matsui1,4
1 Institute of Applied Physics, University of Tsukuba, Tsukuba, Japan; 2 NERC Fundamental Res. Labs., Tsukuba, Japan; 3 LASTI, University of Hyogo, Hyogo, Japan; 4 CREST-JST, Kawasaki, Japan.

We report a successful demonstration of a position control technique for carbon nanotube (CNT) growth catalyzed by an iron nanodot array, which was fabricated by using electron beam induced chemical vapor deposition (EB-CVD). The point irradiation of an electron beam on a resistance gas carbon dot containing iron atoms uniformly dispersed into the dot, and its position could be precisely controlled in the field of a scanning electron microscope (SEM). Vacuum annealing of the ferrocene based dot induced formation of iron nanodots, at a distance of about 10 nm, at an angle of around 60° to the beam irradiation time. We previously reported solid phase graphitization by using such EB-CVD nanostructures, where movement of the iron particles simultaneously induced erosion of the amorphous carbon at the top of the particles and exhaustion of graphite tube at the bottom of the particle[2]. In this paper, we report position controlled carbon nanotube growth with an ethanol CVD process where the nanotubes were catalyzed by iron nanodots on the substrate surface by laser oxidation. We used a conventional scanning electron microscope (SEM) system with a thermal field emitter for a ferrocene based EB-CVD process, which was carried out typically with 180 pA of electron beam at 15 keV. Changing the beam irradiation time for each dot precisely controlled the dot size of decomposed ferrocene. Typically, 1 second of electron beam irradiation produced a dot 5 nm high with a diameter of 80 nm. Vacuum annealing for the dot produced mostly a single iron particle inside it, but amorphous carbon residues with partially graphitized sheets still covered the iron particle. Such amorphous carbon residues were removed using an ashing process in air ambient at 550°C for 30 minutes. After removing the carbon residue, an ethanol CVD process was carried out on the sample at 600°C under 1000 umHg of ethanol vapor incubation. CNT growth from the dots. Many grown CNTs were very thin, being 0.7 to 1.8 nm in diameter, and these diameters were much smaller than the bottom iron particle that was from 2.5 to 5 nm. The growth yield, however, was much higher for the dot than for the tube. The growth yield strongly depended on the surface condition of the SiO2, such as atomic scale scratching and steps, and on the gas flow rate, in particular, the initial increase of the flow rate. References [1] J. Fujita, M. Ishida, T. Ichihashi, Y. Ochiai, T. Kaito, and S. Matsui, Jpn. J. Appl. Phys. 49 (2000) 1379.


Many attempts have been made recently in the direction of anion-doped TiO2 photocatalysis because it has good potential for the utilization of the solar energy to eliminate environmental pollutants in air or water. In this study, N-doped, F-doped, and F-N-codoped TiO2 powders (NTO,FTO, NFTO) were synthesized by spray pyrolysis (SP) from a mixed aqueous solution of TiCl4 and one of the N-precursor (H2CONH2), F-precursor (HF) and F-N-co-precursor (NH4F). An overall comparative study was carried out on these anion-doped powders in order to elucidate the roles of N and F played in visible-light-driven photocatalysis. The comparisons in their experimentally obtained characteristics were based on the analysis of XPS, UV-Vis, PL, NH3-TPD and ESR spectra. The comparisons in their theoretically predicted properties were based on the analysis of the calculated electronic structures. As the results, N-doping into TiO2 resulted in not only the improvement in visible-light absorption but also the creation of surface oxygen vacancies. F-doping produced several additional beneficial effects of charge transfer from O2 to F. For N-doped TiO2, the enhancement of surface acidity and the increase of Ti3+ ions. Doped N atoms formed a localized energy state above the valence band of TiO2, whereas doped F atoms themselves had no influence on the band structure. The photocatalytic measurements showed that the NFTO demonstrated the highest visible-light activity for decompositions of both acetalddehyde and trichloroethylene. This high activity was ascribed to a synergetic consequence of several beneficial effects induced by the N-F-codoping. These findings gained in this study are also helpful for the tailoring of a novel TiO2 photocatalysts with high performances.

O9.5 Studies on Nanoferroelectric Ceramic Based on Nd Doped PZT. R. N. P. Choudhary, S. K. S. Parrashar, Awalendera K. Thakur and B. S. Murty; Physics & Meteorology, I. I. T. Kharagpur, Kharagpur, West Bengal, India.

Nanoferroelectric ceramics have attracted considerable scientific interest because of their unusually improved physical properties having widespread utility in telecommunications, medical imaging, ultrasonic devices and non-volatile memories etc. The impact of the material microstructure on device performance has opened window for developing new methods of material processing leading to an effective control of the sample microstructure to the desired level. This has triggered fresh research on developing new materials having high dielectric permittivity, low loss, tunability of the Curie temperature as per specific requirements etc. It is believed that almost all materials show a crystal size factor is known as critical length, which is normally on nanoscale. The properties of such materials, termed as nanocrystalline, is governed to a greater degree by phenomena such as quantum size effect, surface and interface effects, lattice symmetry, and dependence on the crystal size. The present work aims to investigate crystal size factor effect on the dielectric, ferroelectric and electrical conduction behavior of Nd substituted PZT based nanocrystalline ceramic oxide.

PHYS-0404.0008.ZH.5510.427.958Z3 abbreviated as PnNZT. The material has been prepared by high energy ball milling technique. The procedure enabled us to control the crystallite size to the nanoscale level. The average crystallite size estimated using x ray data, after eliminating the instrumental broadening and Lorentz factor, works out to be ~10nm. This estimate has also been confirmed by transmission electron microscope (TEM) studies. A substantial modification in the XRD pattern of the as mixed powder (green powder) has been noticed on sintering the pellet of mixed powder at 1473K. The dielectric measurements have also shown marked changes in various parameters (permittivity, loss, Curie temperature, polarization behaviour etc.) of the green powder when compared with that of the sintered powder. The results are expected to stimulate further research in the fabrication and design of nanocrystalline dielectric materials for potential applications.

O9.6 Chemical Synthesis and Structure Elucidation of Ultra-high Crystalline Titanate Nanotubes. O-Bong Yang, Mahmood Alam Khan and Hynuchul Lee; Chemical engineering, Chonbuk National University, Jeonju, Chonbuk, South Korea.

Titanium dioxide particles as photocatalytic and photovoltaic materials have been extensively studied owing to its superior physical and photocatalytic properties owing to its high chemical stability, biologically inert, nontoxicity, high photocatalytic efficiency, activity, reactivity, low cost, and chemical inertness. Recently, there are extensive studies on nanostructured tubular materials because of their exceptional physical properties and potential applications in nanoelectronics. Relatively, the titania nanotubes have not been intensively studied, and are not as well known even though the potential advantage to providing direct conduits for photo-excited electrons to the tube channel. TiO2 nanotubes with low crystallinity as compared with high crystalline TiO2 nanoparticles have limitations regarding their application as advanced materials in photo-induced reactions. However, research have been focused on the development of such high crystalline titania nanotubes, despite of their technological importance. In this work, we first demonstrate the simple chemical synthesis of ultrahigh crystalline TiO2 nanotubes as high crystalline TiO2 nanoparticles. Detailed structural and photocatalytical properties of the titanate nanotubes were elucidated. We prepared high surface area Titania nanotube, which was only anatase phase, by hydrothermal method. We used it to augment its crystallinity for the efficient feasibility to its broader photocatalytic and photovoltaic application. The detail structures and properties of nanotubes were characterized by FESEM electron microscopy, HRTEM, X-ray diffraction, TEM/EDX analysis, Photoluminescence, XPS and BET surface area. Thus chemically modified ultrahigh crystalline and high
surface area titania nanotubes showed surprisingly high crystallinity comparable to well known high crystalline Titania nanoparticles. These modified high crystalline nanotube was found to be a multi-walled anatase phase only with an average outer diameter of ~ 8 nm and inner diameter of ~ 5 nm, and well grown along [001] direction to 500 to 700 nm long with the interlayer fringe distance of ca. 0.78 nm. Electrical and structural properties were elucidated and correlated with their photoactivities for synthesized titania nanotubes. To examine the photocatalytic activities of as prepared and modified titania nanotubes, photocatalytic oxidation of triethylbenzene (TEB) gas was carried out under UV (244 nm) irradiation. The photocatalytic activity of modified ultrahigh crystalline titania nanotube was about 2-fold higher than that of titania nanotube as prepared. To our best knowledge, the preparation of ultrahigh crystalline TiO2 nanotubes by controlled chemical treatment has not been known. These noble ultrahigh crystalline TiO2 nanotubes can be applied as highly photocatalytic catalysts, supports, and advanced materials.

O9.7 Electrochemical Synthesis and Characterization of Prussian Blue Nanostructures, Chinglin Tsai1, Sathayoth Ravindran1 and Cengiz Sinan Ozkan1, 2, Mechanical Engineering, University of California at Riverside, Riverside, California; 2Electrical Engineering, University of California at Riverside, Riverside, California; 3Chemical and Environmental Engineering, University of California at Riverside, Riverside, California.

With tricentennial history, mix-valence Prussian blue (PB) exhibits its versatility in several aspects besides being known as an inorganic pigment. The cyanopentahydrated Prussian blue (Prussian blue chloral) electrocatalytic redox sensing, electrochromic, and soft magnetic material. PB thin film has been used in bio-sensors utilizing its redox reaction with hydrogen peroxide. In this article, we reported the fabrication of Prussian blue nanotube (PBNT) and PBNT/PBNW were incorporated into micro/nano patterned electrochemical cell on silicon chip to build a miniaturized PB cholesterol/glucose bio-sensor. The PB cyclic voltammetric measurement confirmed the change of peak current and voltage as the oxygen reduction or hydrogen peroxide generated by analyte. Furthermore, magnetic properties of PBNT/PBNW were investigated by measuring the spin transport through PBNT/PBNW using ferromagnetic materials, such as Ni or Co, as end contact to inject spin into the nanotube/nanowire. The nanowire was integrated by in situ growth at the end of the ferromagnetic electrode. With its magnetic property, PBNW could be a potential building block for spintronic applications.

O9.8 Properties of gas sensor using CNTs thin film prepared by PLD/CVD method. Totsuyoshi Ueda1, Hideyuki Norimatsu2, Mosharraf Hossain Bhuyan2, Tomohito Ibe1 and Kenji Ebihara2; 1Graduate School of Science and Technology, Electrical and Computer Science, Kumamoto University, Kumamoto, Japan; 2Graduate School of Science and Technology, System and Information, Kumamoto University, Kumamoto, Japan; 3Faculty of Engineering, Kumamoto University, Kumamoto, Kumamoto, Japan.

Carbon nanotube (CNT) is a promising material which has potential applications to various nanotechnology devices owing to its unique features like high electrical conductivity, mechanical strength and large specific area surface. Recently, gas sensors using CNTs or carbon nanotube-fiber, which have extremely high sensitivity at a room temperature with fast response, have been reported. Being exposed to oxidizing gas like NO, NO2 or O3, the conductance of the single-walled carbon nanotubes (SWNTs) changes due to charge transfer between the SWNT surface and gas molecules adsorbed. Therefore CNTs will be applicable to gas sensors in various fields. CNTs thin film sensor was prepared and its performance was investigated. CNTs thin film was prepared on a Si(100) substrate using PLD/CVD method. To prepare a sensor device an Al2O3 substrate with Pt interdigital electrodes (sensor substrate) was used. In this method, Fe catalytic thin film was deposited by pulsed laser deposition (PLD) method using Krf excimer laser with power 248 nm, repetition rate 10 Hz, energy fluence 3.3 J/cm². During PLD process the substrate temperature and the ambient gas pressure were kept at room temperature of 25 °C and 3.5x10⁻¹² Torr, respectively. The thickness and roughness of the films were modified by changing the number of ablation laser pulses from 1,000 to 3,000. A small number of laser pulses deposited Fe nano-particles of less than 10 nm in diameter on the substrate. We used 1000 pulses for a catalytic Fe film preparation as small-sized catalyst is necessary to grow SWNTs. CNTs were grown from Fe thin film on Si or sensor substrates by thermal CVD method. Ethanol was used as carbon source. To bubble ethanol and to carry its vapor into the reaction tube, this gas was used and its flow rate was set by a mass flow controller. The substrate was set in the quartz reaction tube heated to 1000 °C in an electric furnace. CNTs were grown for 40 minutes. In our previous studies, it was found that SWNTs can grow under this process. The prepared CNTs were characterized using SEM, TEM and Raman spectroscopy. From SEM observation, randomly oriented CNTs were found on the Si substrate and the sensor substrate. A diameter of CNTs was found to be 10 nm which is proportional to the sensor particle. The Sensitivity of CNT gas sensor was evaluated by measuring the electrical characteristic of the sensor. The gas was exposed to one of the N2, NO, NO2, O3 gases of different concentrations in a chamber. The sensitivity of the sensor was measured by two-terminal method, while the sensor was heated from room temperature to a high temperature on a block heater. The Sensitivity of CNT gas sensors, response time and reproducibility was measured. The relationship between CNTs film properties (length, density and Raman spectra) and sensitivity was investigated. Detail studies and the latest data will be presented at the symposium.


We grew carbon nanotubes (CNTs) using the dc arc discharge process and investigated the synthesis factor of CNTs. Different from the ordinary process, catalyst metal deposited carbon cathode electrodes were used for preparing the CNTs instead of adding catalyst metal powders in a carbon anode electrode. Various transition metal films, applied as catalysts, were used in the experiments. The current density was kept at 10,000 A on a carbon cathode electrode using an e-beam evaporator and an electroplating system. The carbon plasma was generated at various currents from 40 A to 100 A under varying voltage of between 18 - 30 V, and the pressure of the chamber was maintained at approximately 500 torr using a continuous flow of He gas. The flow of He gas around the carbon cathode was controlled by a sheath structure. The cylindrical hard deposits and soot which were collected around the carbon cathode were treated using acidic and thermal treatments to purify the CNTs. Compare with the filtering & centrifugal processes, this process had advantage on the cost and the loss quantity of CNTs. The purified CNTs were characterized by Scanning Electron Microscope (SEM), X-ray Diffractometer (XRD), Raman spectroscopy, and Transmission Electron Microscope (TEM). The experimental results showed that the yield and the morphologies of the grown CNTs varied, depending on the kind of catalyst metal of the carbon cathode electrode. Using the Ni or Co metal film as catalyst, single wall carbon nanotubes (SWNTs) with diameters near 1 nm were mainly detected in the soot collects. But using the Ti film, the SWNTs were not achieved. Besides nitrogen gas, O2 gas was increased in various fields. CNTs thin film sensor was prepared and its performance was investigated. CNTs thin film was prepared on a Si(100) substrate using PLD/CVD method. To prepare a sensor device an Al2O3 substrate with Pt interdigital electrodes (sensor substrate) was used. In this method, Fe catalytic thin film was deposited by pulsed laser deposition (PLD) method using Krf excimer laser with power of 248 nm, repetition rate 10 Hz, energy fluence of 3.3 J/cm². During PLD process the substrate temperature and the ambient gas pressure were kept at room temperature of 25 °C and 3.5x10⁻¹² Torr, respectively. The thickness and roughness of the films were modified by changing the number of ablation laser pulses from 1,000 to 3,000. A small number of laser pulses deposited Fe nano-particles of less than 10 nm in diameter on the substrate. We used 1000 pulses for a catalytic Fe film preparation as small-sized catalyst is necessary to grow SWNTs. CNTs were grown from Fe thin film on Si or sensor substrates by thermal CVD method. Ethanol was used as carbon source. To bubble ethanol and to carry its vapor into the reaction tube, this gas was used and its flow rate was set by a mass flow controller. The substrate was set in the quartz reaction tube heated to 1000 °C in an electric furnace. CNTs were grown for 40 minutes. In our previous studies, it was found that SWNTs can grow under this process. The prepared CNTs were characterized using SEM, TEM and Raman spectroscopy. From SEM observation, randomly oriented CNTs were found on the Si substrate and the sensor substrate. A diameter of CNTs was found to be 10 nm, which is proportional to the sensor particle. The Sensitivity of CNT gas sensor was evaluated by measuring the electrical characteristic of the sensor. The gas was exposed to one of the N2, NO, NO2, O3 gases of different concentrations in a chamber. The sensitivity of the sensor was measured by two-terminal method, while the sensor was heated from room temperature to a high temperature on a block heater. The Sensitivity of CNT gas sensors, response time and reproducibility was measured. The relationship between CNTs film properties (length, density and Raman spectra) and sensitivity was investigated. Detail studies and the latest data will be presented at the symposium.

O9.10 Preparation of Titanium Oxide and Metal Titanates as Powders, Thin Films, and Microspheres by Novel Inorganic Sol-Gel Process. Andrejz Dadl1, Kenneth C. Czajka2, and Maciej Olczak1, W. Lada1, A.G. Chemiewskii3, U. Jakubaszek1, Carlo Alivani1, Sergio Casadigo1; 1Institute of Nuclear Chemistry and Technology, Warsaw, Poland; 2Argonne National Lab, Argonne, Illinois; ENEA, C.R.E. Casaccia, Italy.

Titanium oxide and various titanates are being extensively studied as materials for advanced technologies, such as TiO2 photocatalysts and supports for metallic catalysts, tritium breeders for fusion reactors (Li2TiO4), and cathodes for Li-based batteries (Li4Ti5O12).
Additionally, BaTiO3 and its alloys are widely used in a variety of electronic applications. We report on a preparation procedure for these classes of compounds (including titinates based on Li, Na, K, Ba, or Sr), which utilizes a commercial and inexpensive solution of TiCl4 and HCl. The main preparation steps consist of elimination of chloride anions by distillation with nitric acid, and addition of hydroxides of Al for the formation of Al nanoparticles. The sols were prepared by the following process: produce a doping technique thin films on metallic supports (Ni, Ag, Ti), prepare irregularly shaped powders by evaporation of sols; produce spherical powders (with particle diameter of about 100 micrometers) by solvent extraction of water from sol drops emulsified in 2-ethylhexanol-1. Results of thermal and X-ray-diffraction analyses indicated that the temperatures required to form the various compounds were lower than the temperatures necessary for forming compounds by conventional solid-state reactions. The temperatures of formation could be further decreased by addition of ascorbic acid to the sols.

09.11
The effect of metal clusters on carbon nanotube based sensors. Jeong-O Lee1, Byung-Kye Kim1,2, Hye-Mi So1, Hyunjoo Chang2, Ki-Jeong Kong2, Youngmin Choi2, Ju-Jin Kim2, Noeung Park3 and Byong Hwan Ryu1.1 Advanced materials Div., Korea Research Institute of Chemical Technology, Daejeon, South Korea; 2Department of Materials, Chonbuk National Univ, Chonju, South Korea; 3Department of Applied Physics, Dankook University, Seoul, South Korea.

The electrical transport and chemical sensing properties of single-walled carbon nanotube field effect transistors (SWNT-FETs) coated with metal nanoparticles have been investigated. The current passing through an SWNT-FET coated with Au nanoparticles showed no change over a range of gate voltages. Nevertheless, the magnitude of the current was still sensitive toward NO2, NH3 and H2 evolution. These observations indicated that the secondary structure of the metal-nanotube contacts. Here, the conductance through the nanotube increased, while the trajectory of current around NO2 and NH3 gases improved greatly. We suggest that coating SWNT-FETs with metal nanoparticles could be exploited for the development of highly sensitive nanotube-based molecular sensors.

09.12
EXAFS Study on Nanosized PtRu Catalyst for Direct Methanol Fuel Cell. Hiroaki Nitani1, Takahiro Ono1, Yusuke Honda1, Takashi Nakagawa1, Takao A. Yamamoto2, Hideo Daimon2 and Yukiko Kurobe2. 1Graduate School of Engineering, Osaka University, Suita city, Osaka pref., Japan; 2Development & Technology Division, Hitachi Maxell Ltd., Yawara-mura, Tsukuba-gun, Ibaraki pref., Japan.

In last decade, downsizing and multi-functionalizing of mobile electric devices have been rapidly advanced, and it is strongly demanded to develop power source having high energy density. Direct methanol fuel cell (DMFC) is one of the most promising power sources to be next generation power sources. Nanosized PtRu is utilized as an anode catalyst in DMFC, because it shows excellent CO tolerance. In DMFC, however, effective cell voltage is much lower compared with thermodynamic one due to very high overpotential in methanol oxidation reaction at anode. Therefore, it is essential to improve catalytic activity of PtRu anode catalyst for realization of DMFC. In this report, catalytic activity of nanosized PtRu anode catalyst is described. EXAFS analysis demonstrates that there exists an arrangement of Pt and Ru atoms in PtRu catalyst showing different catalytic activity. PtRu catalysis was synthesized by polyol process using ethylene glycol as reducing agent. Mixture of carbon support, Pt and Ru precursors and ethylene glycol was refluxed at 473 K for 4 hours with mechanical stirring under nitrogen atmosphere. Before refluxing, pH of synthetic solution was adjusted to 3.0 and 5.5 by adding sulfuric acid. Catalytic activity of PtRu catalyst for methanol oxidation was measured by linear sweep voltammetry (LSV). Comparison of Pt and Ru catalyst structure and morphology of PtRu catalyst were examined by XRF, XRD and TEM. Pt-L3 edge EXAFS spectra of PtRu catalyst were obtained at the BL-7C beam line of KEK-PC. LSV measurements showed that PtRu catalyst synthesized at pH 3.0 has higher catalytic activity for methanol oxidation reaction compared with one synthesized at pH 5.5. Methanol oxidation currents at 0.4 V (vs. NHE) were 8.43 mA and 2.43 mA, respectively. XRF, XRD and TEM analyses further show that a significant distinct difference between these two catalysts. EXAFS analysis found that there is no significant difference in coordination number of Pt-Ru bonding. Coordination numbers of Pt-Ru bonding in PtRu catalysts synthesized at pH 3.0 and at 5.5 are 1.4 and 0.6, respectively. This result indicates that Pt and Ru atoms in PtRu catalyst synthesized at pH 3 exist more uniformly compared with PtRu catalyst synthesized at pH 5.5. It is well known that Ru is a better catalyst for oxidation of chemisorbs on active site of Pt. Based on bifunctional mechanism, it is expected that Pt and Ru atoms exist contiguously either for oxidation of CO by hydroxyl functional group generated on Ru, or for O2, LSV measurement and EXAFS analysis on PtRu catalysts. It is found that Pt and Ru atoms stand close shows higher catalytic activity for methanol oxidation reaction, which strongly supports bifunctional mechanism. Recently, it was found that size of PtRu anode catalyst is reduced by 2 nm by addition of ex-situ deposited Pt. Effect of PtRu on catalytic activity for methanol oxidation reaction is also discussed.

09.13

We have developed a novel catalytic process to yield a novel carbonaceous material, named Marino Carbon, by using diamond supported-Ni, Co, and/or-Pd catalysts. Ni, Co, and/or Pd were loaded onto the oxidized diamond powders which were <500 nm in size by an impregnation method from such corresponding metal aqueous solutions. The diamond supported catalysts were reduced in to the fluid-bed chemical vapor deposition reactor with an outer electrical heating system. Methane was fed into the reactor and decomposed onto the diamond catalysts. The diamond supported metal catalysts in the temperature range from 525 to 700 °C to yield silicon filamentous materials. No reaction can proceed without the diamond supported catalysts. The fine diamond powder played as a catalyst support and a nucleus for a filamentous carbon deposition. The secondary supported metal catalysts were produced onto the small catalysts on the diamond supports. Their diameters were 1 to 100 nm, with several micro meter lengths. Plenty numbers of carbon filaments were grown on the diamond nanosized substrates, and the filamentous carbon structure were like the Marino. The Marino carbon were formed to be spherical-ball shape which diameters were 1 to 10 micro meter in this study. The secondary diameter was related to the reaction time. The Marino carbon were a large specific area and mechanic strength with a very low density and weight. It is expected to be applied as a new catalyst support, a substrate for dielectric capacitors, a new electrode material for fuel cells, a new carbon component for complex composite materials.

09.14
Preparation and characterization of thin films by pulsed laser deposition for NOx gas sensor. Md. Moshrur Hossain Buiyan1, Tomyoshi Ueda1, Keiji Shingi1, Tomoaki Iegami2 and Kenji Ebihara2. 1Graduate School of Science and Technology,Department of Systems and Information, Kumamoto University, Kumamoto, Japan; 2Department of Electrical and Computer Engineering, Kumamoto University, Kumamoto, Japan.

Tungsten trioxide (WO3) based materials as sensors for monitoring of environmental gases such as NOx have been developed for various practical applications. The sensing mechanism lies in the changes of film resistance resulting from physisorption, chemisorption and catalytic reactions of gas phase species with the film surface. It has been reported that these materials are highly sensitive to NOx with the sensitivity further enhanced by adding precious group metals (PGM such as Pt, Pd, Au, etc.). In particular, the role of promoter is not yet clear though speculations on their catalytic, electronic and structural effects have been made in the past. In parallel to these PGM promoters Ag promoter can also enhance the sensitivity of WO3 thin films significantly. The gas sensors based on WO3 thin films doped with different amount of platinum (Pt) or gold (Au) or palladium (Pd) were synthesized by KrF excimer laser pulsed laser deposition method with dc sputtering. The films were deposited on silicon, quartz and Al2O3 substrate with Pt interdigital electrodes at different substrate temperatures, oxygen pressures. Nitrogen and oxygen gases were also used at different rates. Before deposition, the chamber was pumped down to a base pressure of 1.5x10-5 Torr. The targets (WOx, WOx-Pt, WOx-Au, WOx-Pd, WOx-Ag, Dowa, purity=99.99%, 30mm) were ablated by KrF excimer laser (Lambda Physik Lasergeneratorsche, maximum energy=650 mJ, λ=248 nm, pulse duration=25 ns) with the repetition rate of 10 Hz for 10 minutes. The distance between the target and the substrate was 5-6 cm. The substrate temperature and the oxygen pressure were changed from 300°C to 500 °C and from 100 mTorr to 500 mTorr.
Instruments Inc. SP13800N). The optical transmission of prepared films was measured using a spectrophotometer (Ocean Optics). To evaluate the structural stability of the catalyst, the thickness of the WO 3 thin films was measured by a two terminal resistance method in a chamber. The sensitivity of the WO 3 thin films was calculated from the resistance in the NO gas. The flow of NO gas was adjusted by mass flow controller. The WO 3 thin films sensor was kept to a range of temperature from 200°C to 600°C by an electrical block heater with a temperature controller. The sensitivity of the WO 3 thin films gas sensors with doping (PdM or Ag) was found to be higher than that of the WO 3 thin films. Without the structure provides by the microarrays, thin films doped with NO 2 and also SnO 2 gas sensors doped with carbon nanotubes (CNTs). The latest experimental results will be submitted in the 2005 MRS symposium proceedings.

**09.15 Liquid Phase Deposition of Carbon Nanomaterials by Using a Cobalt Catalyst, Takeshi Shibasaka 1, Hidetomi Gano 2, Kiyoharu Nakagawa 3, Yoshihiro Ando 3 and Mikka Nishitani-Gamo 3**

The development of a new catalytic method for the control of carbon nanomaterials was investigated in this study. **Cobalt** catalysts were used to control the growth of carbon nanomaterials, which consists of a quartz chamber with an outside coating. The morphology of grown materials was observed by Scanning Electron Microscopy (SEM). The structure of grown materials was observed by Transmission Electron Microscopy (TEM). The observation revealed that the morphology of the grown materials depended on the reaction temperature. Under the reaction temperature in the range from 600 to 700°C, fibrous deposits were mainly obtained. In the range from 800 to 900°C, particles of about 10 nm in diameter deposits were mainly formed. Above 1000°C, film-like carbon materials were grown on the substrate surface. We observed TEM images of the fibrous carbon growth with a different thickness of the catalyst film. The more increase of the Co film thickness, the more thickness of filament diameter. The fibrous carbons grown with 1 nm thickness of Co have little coixial follow channel. In contrast, the grown materials with 3 and 6 nm thickness of Co have effective coixial channels; the density of the catalyst could be further increased by using carbon nanotubes. The amount of supported catalyst affects structure of the grown fibrous carbon. A chemical and/or physical surface of the catalyst is one of the effective parameter for the growth and structure of the materials. References: 1) T. Ando, M. Nishitani Gamo, F. Y. Zhang, PCT/JP92/09235, 2) Y. F. Zhang, M. N. Gano, C. Y. Xiao, and T. Ando, Jpn. J. of Appl. Phys., 41, L408-L414 (2002).

**09.16 Functionalization of 3-D Structures for Grafting of Biological Molecules, Cecile Ollier 1, P. Mun 2, E. Blanquet-Nicolas 2, G. Delapierre 1, F. Vinet 1 and T. Billon 1**

DNA microarrays are considered as powerful tools, allowing massively parallel analysis of biological processes and therefore a reduction of time analysis. The functionalization of the surface is a key step in the preparation of the microarray. Thin films materials with specific surface properties are useful for these applications, in particular for covalent immobilization of various biomolecules such as nucleic acids and proteins. Even though most microarrays present good quality, accuracy and reliability, they lead to a planar surface structure, which neither enough increases the accessibility of the targets to the probes nor the loading capacity of the solid support. Moreover, due to the low amount of biological samples, the sensitivity and the reliability of tested signal becomes major problems. To achieve a high density of reactive functions, the use of a non-planar nanostructured surface is investigated as an available surface area for grafting of biomolecules. We propose to build up a pseudo-three-dimensional structure, covered with a specific layer, and then submitted to various chemical steps. Two kinds of reactive silane chemistry allow forming the surface of the samples. The first one is carried out in a vapour phase and the second one in a liquid phase.

Both silanisation methods allow to introduce of a large number of aldehyde functions at the periphery of the substrates, leading to covalent and non-covalent-modified optical and electronic probes on the reactive layer of the support. The performances of the microarrays silanised by the two presented methods are investigated by means of hybridization experiments using complementary fluorescent labelled oligonucleotides and the targets. Our results indicate that these novel surfaces provide an increase of available specific surface leading to a high binding capacity of the support for amino-modified oligonucleotides compared to the results obtained with a planar surface structure. The silanised surfaces without the structures present a higher specific surface area for attaching biomolecules which will increase the density of biomolecules and hence, the sensitivity for detection. As a consequence, they could confer a higher accessibility to the targets, allowing to reduce the limits of detection upon hybridization and to enhance the intensity of the fluorescent signal, proportionally to the increase of available specific surface. The novel surfaces prepared in the vapour phase, a solvent free process, show interesting surface properties, like a thinner deposited layer and therefore a better conformation of the support. Moreover, the grafting of biological molecules and the detection of the hybridization with the complementary targets can be carried out on these surfaces.

**09.17 Optical Gas Sensor Using Cobalt Oxide Thin Film Prepared by Pulsed Laser Ablation, Hyun Jeong Nam, Takeshi Sasaki and Naoto Koshizaki**

Gas sensors based on optical absorption changes in thin films are of interest for detection of various gases such as CO, NO, H 2. Optical gas sensors have several advantages over conventional electronic gas sensors, including the potential for higher sensitivity, reduced signal noise, and compatibility with combustible gases. Pulsed laser deposition (PLD) is an excellent method to prepare thin films with controllable thickness, composition and microstructures. Recently, our group reported that films of cobalt oxide prepared by PLD exhibit remarkably high sensitivity, showing an absorbance change in CO gas 70 times greater than those prepared by sputtering methods. We examine the effect of film microstructure and composition on CO gas sensing properties in order to identify the origin of the high sensitivity. The films were prepared by PLD on a Co target in an inert argon gas at various pressures. Films prepared near vacuum were smooth and continuous while the porosity and grain size increased linearly with pressure. In addition the pressure affected the composition and the thickness of the films. Data on the detection of CO gas suggests a direct relationship between sensitivity to CO gas and the effective surface area of films. We will discuss how the ablation plume can be used to tune the surface area for optimal sensitivity, and will demonstrate origin of the high detection sensitivity based on the structural changes with detecting gas. 1) Leszek Zbroieniec, Takeshi Sasaki and Naoto Koshizaki, Technical Digest of the 10th International Meeting on Chemical Sensors, Tsukuba, Japan (2004) p.358-359; 2) Masanori Ando, Tetsuhioko Kobayashi, Sunio Iijima and Masakata Haruta, J. Mater. Chem., 7 (1997) 1779-1783.

**09.18 Preparation of Cu-SiO 2 Nanoparticles and Study of Antibiotic Property, Young Soo Kang and Young Wun Kim**

A room temperature route for doping silica particles with Cu nanoparticles to achieve hybrid structures is introduced. First, silica nanoparticles were synthesized according to the well-known St öber method by hydrolysis and condensation of TEOS in a mixture of ethanol with water, using ammonia as catalyst to initiate the reaction. These SiO 2 nanoparticles were dried at 100°C. We measured the size of these nanoparticles with transmission electron microscopy (TEM). Second, CoSiO 2 nanoparticles were synthesized by the reaction of CuCl 2 and SiO 2 nanoparticles at a reaction temperature of 12 hrs. Results show silica nanoparticles of about 60 nm size with regularly deposed Cu nanoparticles. Cu-SiO 2 nanoparticles were investigated with TEM images, energy dispersive X-ray analysis (EDX) spectrum and so on. In this study, we will investigate the results of Cu-SiO 2 nanoparticles applied to antibiotics.

**09.19 Thermally Grown Aligned Carbon Nanotubes on SiC Fibers for Electrochemical Applications, Bill Logan Riehl 1, Michael Check 1, John Bocek 1, William Mitchell 1 and Elmo Blubaugh 1**

Aligned carbon nanotubes have recently become the focus for a resurgence in the chemical and biological sensors research field. This
is largely due to the promising behavior of nanotubes when in ohmic contact to an electrical conductor. By building arrays of aligned carbon nanotubes, a large surface area of nanotubes can be had, with surface areas approaching or exceeding that of activated carbon or porous catalyst substrate. These attributes, when combined with the rapid electron transfer rates and the ability to readily undergo redox reactions, have made nanotubes a common support for enzymes and other catalysts.

Bimetallic nanoparticles and their ensembles exhibit interesting electronic, optical, and chemical or biological properties due to bifunctional coupling effects. The interface between metal species of gold/bimetallic nanoparticles for catalytic reactions have recently been studied. While the preparation of AuAg nanoparticles has been reported, the synthesis of the bimetallic nanoparticle system with both compositions and size controllability in a wide range has not been established. At the same time, this knowledge about assemblies of binary or ternary metal nanoparticles, which is in part due to the lack of strategies for controllable interparticle linkages. This presentation describes a new strategy in the synthesis and assembly of monolayer-capped binary gold-silver (AuAg) bimetallic nanoparticles. One goal is to understand the nanoscopic properties of the bimetallic nanomaterials for chemical/biological sensing and catalytic applications. The synthesis of alkane/thiol-capped AuAg nanoparticles was carried out using a two-phase reduction of AuCl4- and AgBr2- both of which are, separately, first transferred into organic solution. The assembly utilizes the unique interparticle-linking chemistry of dinonfunctional groups at Au and Ag sites for defining the interparticle chemistry. The nanostructured thin film assemblies were tested for sensing volatile organic compounds using chemiresistors transducers. In this section, we will explore the assembly of the nanostructured bimetallic nanoparticles for constructing sensing arrays and catalytic nanomaterials will also be discussed.

Q0.21 Abstract Withdrawn

Q0.22 Magnetic Nanocomposite Films of High Temperature Polyimides. Sang-Hyon Chu1,2, Keun J. Sun1,2, Min Namkung2, Russell A. Wincheski3 and Ruth H. Pater2; 1National Institute of Aerospace, Hampton, Virginia; 2NASA Langley Research Center, Hampton, Virginia.

The purpose of the present study is to develop magnetic nanocomposite films with excellent magnetic sensitivity, permeability, and material stability, by incorporating magnetic nanoparticles into high-temperature polyimide. NASA Langley Research Center. The high temperature polyimides exhibit high mechanical strength and structural durability at elevated temperatures, while maintaining significantly less moisture absorption and therefore high performance and high stability. This excellent material properties make the polyimides ideal as the matrices of advanced functional materials not only for NASA’s aerospace applications but also for many commercial applications that require light-weight and high-performance. There is an increasing interest in developing advanced nanocomposite materials because of their unprecedented material properties. Magnetic nanoparticles have received much attention in this regard, because of magnetic domain size effects and potential applications for magnetic sensors and devices. A critical obstacle in developing a nano-structured composite material is its tendency to aggregate. Creating magnetic nanoparticles from iron chloride solutions followed by mixing them into a desired matrix is one of the popular strategies to fabricate a magnetic nanocomposite material. For more practical applications, however, the present study is focused on developing the magnetic nanocomposite films by exfoliating nanoparticles that are uniformly dispersed and commercially available. This approach brings more challenge in terms of nanoparticle dispersion but it can be applied to a wide range of nanoscale systems such as semiconductor nanocrystals, carbon nanostructures, high dielectric materials, etc. In this study, to avoid the aggregation problem, various synthesis techniques were employed including in-situ polymerization which allows the polyimide monomer reaction to enhance the multiphase miscibility and the separation of the magnetic nanoparticle. The synthesis procedure is described and successful produced high performance flexible nanocomposite films as final products. The nanocomposite films with various volume fractions of the magnetic nanoparticles were analyzed by high resolution field emission SEM and magnetic force microscopy for the nanostuctures of the magnetic films. FTIR spectroscopy and differential scanning calorimetry were used for charaterizing and identifying molecular structure of the nanocomposite films. The magnetic properties of the films containing the magnetic nanoparticles were also characterized at various temperatures using SQUID magnetometer and vibrating sample magnetometer. Along with the enhanced magnetic sensitivities, the solution-based film fabrication in this study should allow for the application of conformal coatings on various surfaces and the creation of patterns of various size and shape in the potential sensor applications.

Q0.23 Mechnochemical Synthesis, Structural Characterization and Visible Light Photocatalysis of TiO2/2ZnFe2O4 Nanocomposites. Jasdeep Singh1, Nauna Raw9, Nikhil Kishor1, Matthew T. Smith5, Elias Lee Stefanakos1 and Yogi Goswami2; 1Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida; 2Solar Energy and Energy Conversion Laboratory, College of Engineering, University of Florida, Gainesville, Florida.

Nanocomposite heterogeneous semiconductors with suitable energy levels (gaps) are exhibiting excellent photocatalytic properties under visible light irradiation. The wide range of semiconductor materials has been selected among different alloys because of (i) its low band gap ~1.9 eV (ii) the nontoxicity of ZnFe2O4 (iii) visible light absorption characteristics of ZnFe2O4 due to its narrow band gap and (iv) not being susceptible to photocatalytic corrosion. The nanocomposite was synthesized via chemical reduction method using high energy milling is employed to prepare TiO2/ZnFe2O4 under different experimental parameters and conditions. The as-milled nanocomposite materials are characterized with XRD, SEM and EDS procedures. The photocatalytic activity of TiO2/ZnFe2O4 nanocomposites for the photodegradation of phenol under visible light irradiation has been studied systematically by UV-Vis spectrometer.

Q0.24 Study of Crystal Structure and Thermal Stability of Layered Sodium-Titane Nanotubes. Paula Mendes Jardim1, Bojan Marinovic2, Edisson Morgado3, Marco Antonio Santos de Abreu2 and Fernando Rizzo1; 1Materials Science and Metallurgy Research Center, Rio de Janeiro, RJ, Brazil; 2PETROBRAS Research Center, Rio de Janeiro, RJ, Brazil.

Titannate NanoTubes (TNT) with high surface area and reasonable thermal and hydrothermal stability are interesting candidates for catalytic applications. Single-crystal nanotubes are generally prepared from layered structured materials. It was surprising when Kasuga et al [1] reported the synthesis of Titania single crystal nanotubes prepared from anatase powder by hydrothermal treatment as the crystal structure of anatase is not layered. Various contradictory studies have been reported on the crystal structure of these Nanotubes. Actually, there are four different crystal structures proposed in the literature, namely: hydrated titanate with hydroxidoclate-like structure, titratitanate, hydrated tettatanatate and anatase. Studies on thermal and hydrothermal stability of single crystal titania nanotubes are not so common in the literature. Furthermore, the synthesis of such nanotubes with nominal composition ascribed to H1.5Na0.5Ti3O7 have been studied and their poor thermal stability reported with decomposition into anatase around 550°C. In the present work Sodium-Titane single crystal nanotubes were prepared following the Kasuga method and the crystal structure and thermal stability were investigated. The samples were prepared by hydrothermal treatment of titania powder in NaOH 15M at 120°C for 15h, followed by washing with HCl/H2O (pH=7). In Situ X-Ray Diffraction (XRD) of the as-prepared sample was performed from room temperature to 900°C. The as-prepared and heat-treated samples were analyzed by Transmission Electron Microscopy (TEM), Electron Energy Loss Spectroscopy (EDS) and Electron Diffraction (ED). EDS analysis showed that as-prepared nanotubes are Na-rich. Therefore, it was assumed that Na is incorporated in the nanotube crystal structure. In Situ XRD analysis demonstrated that the nanotubes remained up to at least 600°C, transforming at around 700°C into Na2Ti6O13.

**09.25** Photocatalyst Application of ZnO Nanorods. Jib-Jin Wu and Chien-Hao Tsai, Chemical Engineering, National Chiang Kuo University, Taian, Taiwan.

Highly oriented ZnO nanorods have been grown on various substrates using a simple catalyst-free MOCVD method at low temperatures. In comparison with ZnO film, the ZnO nanorods possess much better photocatalytic activity for degradation of methyl orange (MO) under 365 nm irradiation. According to Langmuir-Hinselwood model, the apparent 1st-order reaction rate constant is enhanced 2 orders of magnitude. To further enhance the photocatalytic activity, photocatalytic deposition of noble metal nanoparticles, such as Ag, Au, and Pt, on the ZnO nanorods has been performed using photocatalysis method under 365 nm irradiation. Metal particle sizes and densities can be controlled by deposition times and the concentrations of the noble metal precursor solutions. It reveals that the photocatalytic activities of the nano-metal/ZnO nanorod composites for MO degradation depend on the density and the size of the metal particles on the ZnO nanorods. The mechanism for the enhancement of the photocatalytic activity by forming nano-metal/ZnO nanorod composites will be discussed in this paper.


One-dimensional (1-D), metal oxide (ZnO, SnO2, TiO2) nanostructures were synthesized in solution without using any surfactants or capping agents. The aspect ratios (length/diameter) of these 1-D nanostructures can be tuned by deliberately selected growth conditions (precursor concentrations, reaction temperature and time etc.). These nanorods were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED). The optical properties were also measured. And furthermore, these novel reaction systems for making group of 1-D nanostructures provide an interesting direction to study the fundamental nucleation, growth of metal oxide anisotropic nanocrystals.

**09.27** Catalytic Effects and Characterization of Ni-based Catalysts Supported on TiO2-SiO2 Xerogel for Oxidation of Acetone/Alcohol. Jong-Woo Jeong1, Jong-Hui Park2, and Chang-Seop Lee3,1Chemistry, Keimyung Univ., Daegu, South Korea; 2Chemistry, Graduated school, Keimyung Univ., Daegu, South Korea.

The catalytic activities of nickel-based catalysts were estimated for oxidizing the acetaldehyde of VOCs exhausted from industrial facilities. The catalysts were prepared by sol-gel methods of SiO2 and TiO2-TiO2 as a xerogel followed by impregnating the Al2O3 powder with the nickel nitrate precursor. The crystalline structure and catalytic properties for the catalysts were investigated by using BET surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR) techniques. These results show that nickel oxide is transformed to the NiAl2O4 spinel phase at the calcination temperature of 673K in response to the steps with after- and co-impregnation of Al2O3 powder in sol-gel process. The NAI2O4 could suppress the oxidation reaction of acetaldehyde by catalysts. The NiO is better dispersed on SiO2-TiO2/Al2O3 than on SiO2/Al2O3 and SiO2-TiO2/Al2O3 support. From the testing results of catalytic activities for oxidation of acetaldehyde, catalysts they showed a big difference in conversion efficiencies with the way of the preparation of catalysts and the loading weight of nickel. The catalyst of wt.% Ni/1TiO2-SiO2/Al2O3 showed the best conversion efficiency on acetaldehyde oxidation with 100 % conversion efficiency at 623K.

**09.28** Reactions of Organohalogens with Zero-valent Sodium (Na0) Treated Fajusite Zeolite at Room Temperature. Charles Wairagu Kanyi and David C. Doetschman; Chemistry, Binghamton University, Binghamton, New York.

The conversion of carcinogenic or mutagenic organohalogenes to less environmentally hazardous materials is desirable. Presently, this involves one of three processes: thermal decomposition, oxidation and hydrodehalogenation, processes that involve formation of toxic (dioxins) by-products. Na0 treated fajusite zeolites2 decompose organochlorines at room temeperature. Using transmission electron microscopy (TEM), liquid ITR NMR and solid state 13C NMR, we reported decomposition of methyl iodide, ethyl iodide and ethyl bromide. Methyl iodide in Na0 activated NaX and NaY decomposes to form a framework stabilized methyl group (O-CH3) C=O chemical shift at 167 ppm. Gaseous products, methane and ethane were found using IR and GC-MS. In activated NaY an additional small amount of strongly bound methanol (49 ppm) was detected. Comparatively, larger amounts of methane and methanol products were observed for activated NaX than in NaY. Ethyl iodide and bromide formed framework ethoxy and ethene gas. Proposed nucleophilic reaction mechanisms for above products will be discussed.

**09.29** Effects of Microstructural Parameters on the Sensor Performance of Tin Oxide Nanoparticle Microshell Films. Carlos J. Martinez, Bernard Hocking, Christopher Montgomery and Steve Semancik; National Institute of Standards and Technology, Gaithersburg, Maryland.

We have sought to gain a fundamental understanding of the influence of microstructural parameters on the sensor performance of tin oxide nanoparticle microshell films. These films were fabricated via the sol-gel method from solution of nanoparticle-dispersed langasite microspheres, which serve as sacrificial templates. Single and multiple oxide layers were developed via the sequential electrostatic adsorption of oppositely charged polyelectrolytes and tin oxide nanoparticles on the surface of latex microspheres. Through laser heating, the latex microspheres were removed to reveal a multilayered 3-dimensional structure composed of interconnected hollow nanoparticle microsells with ultra-thin walls. Three microstructural parameters were varied in these studies. The microshell diameter and thickness were changed by varying the latex microsphere diameter and by adsorbing multiple nanoparticle layers on the microspheres, respectively. The film thickness was changed via successive deposition from solution using a microspipette. In particular, we were interested in understanding how these parameters affected the number of available sites for gas adsorption and the diffusion rates of analytes to reach these sites. To assess the sensing characteristics of these different structures, sensor measurements were performed after these films were deposited onto MEMS microsensor platforms with embedded heaters and inter-digitated electrodes. We determined the sensitivity, speed and stability of these films for sensing by measuring the conductance changes, at different temperatures, caused by exposure to test gases (carbon monoxide, water and methanol) in a dry air background. The response characteristics were examined for target analyte concentrations in the range of 80 nmol/ml (ppb) to 100 µmol/ml (ppm). Films composed of (1-D) nanoparticle microsells exhibited the highest baseline conductance and were shown to be structurally stronger during the core removal process. We also noted that films composed of the largest diameter (1-D) nanoparticle microsells exhibited the most sensitivity for all gases tested, in particular to methanol. This suggests that analyte diffusion may be the rate limiting step in the transduction process for these films. Overall however, these open structures offer enhancements in sensitivity for all the gases tested when compared with more compact nanostructured tin oxide films.

**09.30** Structural and vibrational properties of vanadate nanotubes. Antonio Gomes Souza1, Elton J. G. Santos1, Josue Mendes1, Odair P. Ferreira2 and Oswaldo L. Alves2, 1Faculdade Universidade Federal de Ceará, Fortaleza, Ceará, Brazil; 2Quimica, UNICAMP, Campinas, Sao Paulo, Brazil.

In this paper, we report a detailed study of structural and vibrational properties of vanadate nanotubes (VONTs). We have identified the Raman-spectral signature of the tubular structure beside the Raman bands characteristic for both dodecachromine- and Cu-intercalated VONTs. The spectra are characterized by peaks at 102, 250 and 910 cm⁻¹. We also have investigated the temperature effects on the vibrational and structural properties of VONTs by changing the laser power density during the Raman measurements and measuring the FTIR spectra of the samples decomposed at different temperatures. We have found that the tubular structure is sensitive to the temperature effects and that the decomposition of the tubes into V2O5 oxide is an intermediate compound that is isostuctural to V2O5 xerogel. The irreversibility of the decomposition process is confirmed by observing the color changes at the laser spot. The laser power density threshold necessary for decomposing the VONTs into V2O5 oxide depends on the intercalated species. Therefore, one should be very careful in getting
the Raman spectra of VONTs because the local heating effect due to the laser easily convert the nanotubes into V2O5 oxide. Our study allowed to establish the Raman signature of the VONTs and that this technique is powerful and useful as an easy quick tool for probing VONTs samples.

O9.31

**Nanosecond characterization of Pd/TiO2 catalysts and Ag/TiO2 catalysts by electron holography.** Satoshi Ichikawa1, Tomoki Akita2, Kazuyuki Okazaki3, Koji Tanaka4 and Masanori Kohyama4.

1Graduate School of Engineering, Tohoku University, Sendai, Japan; 2Department of Nanotechnology, Osaka University, Toyonaka, OSAKA, Japan; 3Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan.

Catalytic properties of noble metal catalysts are often caused by their nanostructures and the interaction between nano particles and oxides supports. Anomalous results show the size dependence of catalytic activities owing to the change of the local electronic structure of Au particles and the strong interaction at the interface between Au particles and TiO2 supports. We applied electron holographic and high-resolution electron microscopic techniques to Au/TiO2 catalysts, and found that the mean inner potential of Au particles supported on TiO2 increases depending on the size of Au particle when the size is smaller than 5nm. The size dependent behavior of the mean inner potential of Au in Au/TiO2 catalysts is similar to that of the catalytic activity in Au/TiO2 catalysts. In the present study, we examine the mean inner potential of Pd particles in Pd/TiO2 and Ag particles in Ag/TiO2 catalysts using electron holography and HREM. And we compare the results of the Pd/TiO2 and Ag/TiO2 systems with our previous results of the Au/TiO2 and Pt/TiO2 systems. In the case of the Pd/TiO2 catalysts, when the size of Pd particle is smaller than 5nm, the mean inner potential of Pd changes to be higher than the calculated value of the mean inner potential which is thought to be larger than the experimental values of bulk Pd by 3-5V. The mean inner potential of Pd becomes to increase gradually as the size of the Pd particle decreases. The rate of the increment in the mean inner potential of Pd is lower than that of Au/TiO2 catalysts and Pt/TiO2 catalysts. On the other hand, in the case of Ag/TiO2 catalysts, the mean inner potential of Ag does not increase but slightly decrease though the size of the Ag particles decreases to understand the reason of the difference of the work function is one of the reasons that the size dependence of Ag/TiO2 system exhibits the peculiar behavior.

O9.32

**Catalytic and Physical Properties of Copper-Manganese Oxides Catalysts Supported on γ-Al2O3 for Toluene Oxidation.** Iye-Jin Kim1, Sung-Woo Choi2 and Chang-Seop Lee1.

1Environmental Science & Engineering, Graduate school, Keimyung Univ., Daegu, South Korea; 2Environmental Science & Engineering, Keimyung Univ., Daegu, South Korea; 3Chemistry, Keimyung Univ., Daegu, South Korea.

The catalytic incineration of toluene over γ-Al2O3-supported copper-manganese oxides catalysts in the temperature range of 433-553K was investigated by employing a fixed bed flow reactor. The catalysts were prepared by BET, XRD, Raman, Scanning Electron Microscopy (SEM), Temperature-programmed reduction (TPR), Temperature-programmed oxidation (TPO), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) techniques. Incineration of toluene was achieved in the 553K, or below region and the optimal content of metals of catalysts turned out to be 10.0wt.% Mn-15.0wt.% Cu on γ-Al2O3. BET results indicate that surface area have no relationship with activity of catalysts. TPR/TPO results showed that redox peak of 10Mn-15Cu catalyst shifted to lower temperature and XPS results showed that binding energy of metals shifted toward higher energy. From the XRD results, we assumed that Cu1.5Mn1.5O4 is an active site of catalysts and it appears to be responsible for the redox ability of catalysts and high oxidation state.

O9.33

**Template-based electrochemical method for multi-segmented metallic nanotubes.** Woon Lee, Roland Scholtz, Konradus Niehuis and Ulrich Goesele: Max Planck Institute of Microstructure Physics, Halle, Germany.

Tubular nanostructures have stimulated extensive research efforts in recent years because of their technological importance in advanced electronic or magnetic devices and applications in catalysis, sensors, and biological separation/transport. Recently, we have developed a novel and practical approach for preparing arrays of nanotubes embedded in alumina templates, which can be readily extended to a wide range of metallic or semiconducting materials. The method is based on the preferential electrodeposition of a metal along the pore walls of an anodic aluminum oxide (AAO) membrane in the presence of metallic nanoparticles on the nanochannel surfaces. We utilized the well-established redox cycling between Ag(I) and Ag(0) in order to immobilize Ag nanoparticles on the surface of alumina nanochannels, where surface bound Sn(II) ions spontaneously reduce Ag(I) into Ag(0) (i.e., 2Ag(I)(aq) + Sn(II)(aq) -> 2Ag(0)(aq) + Sn(II)(aq)). By taking advantage of precise control of the growth of the metal nanotubes, we were able to prepare for the first time noble multi-segmented metallic nanotubes with bimetallic stacking configurations (e.g., Au-Ni-Au) along the nanotube axes by employing sequential electrodeposition. We assume that the present electrochemical preparation of the nanotubes with heterostructural architectures can enable us to combine two or more desirable materials properties. Due to the potential modulation of the surface properties along the tube axis, various functions materials (e.g., proteins, DNA) can be assembled to the defined sites of the inner or the outer tube surface. Therefore, it is expected that our multifunctional nanotubes are potentially useful in the field of catalysis, advanced microfluidics, biological and magnetic sensors, as well as molecule separation. In this presentation, magnetic properties of the metal nanotube will also be discussed. Financial support from the German Federal Ministry for Education and Research (BMBF, Project No. 03N8701) is greatly acknowledged.

O9.34

**Nanocrystalline MgFeOx (M = Cu, Fe, Mn, Ni, Zn) aerogels as magnetic nanoarchitectures.** Katherine Ann Pettigrew1,2, Jeffery W. Long1,3, Everett E. Carpenter2, Rhonda M. Stroud2 and Debra R. Rollison1.

1Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; 2Chemistry, Virginia Commonwealth University, Richmond, Virginia; 3Materials and Sensors Branch, Naval Research Laboratory, Washington, District of Columbia.

We have developed MgFeOx (M = Cu, Fe, Mn, Ni, or Zn) aerogels that exhibit magnetic behavior while retaining the continuous pore-solid network and monolithic nature of an aerogel structure. [1] The synthetic methods of Gash et al. [2] have been adapted to form amorphous MgFeOx aerogels that are then transformed under controlled temperature and atmosphere into nanocrystalline magnetic oxides that exhibit superparamagnetism to ferromagnetism. X-ray diffraction patterns of the nanocrystalline aerogels are consistent with spinel MgFeOx, confirming that Mg1+ from the initial sol-gel mixture is incorporated within the crystal structure of the resulting oxides. Transmission electron microscopy confirms crystallinity and establishes particle size, morphology, and elemental composition of the various aerogels. These magnetic solids retain the inherent characteristics of aerogels: high surface area, through-connected porosity in the mesopore (2-50 nm) range, and nanoscale particle sizes. Based on our demonstrated ability to control both the pore-solid architecture and the nanocrystalline phase of these mixed-metal iron oxides, we are now able to design novel magnetic nanoarchitectures. Of particular interest will be the interaction of guest ions and molecules within the magnetic nanoarchitectures, with potential applications for sensing and separation. We are also developing these materials as ion-insertion electrodes and as high-surface-area supports for heterogeneous catalysis. [1] J.W. Long, M.S. Logan, E.E. Carpenter, and D.R. Rollison, J. Non-Cryst. Solids, 304-305, 182 (2004); [2] A.E. Gash, J.M. Bliatou, A. Duerer, J.F. Poco, L.W. Hrubesh, and R.L. Simpson, Chem. Mater., 13, 999 (2001).

O9.35

**Sub-micron Patterning on Polymer Films for Protein Arrays.** Karen L. Christman1,2, Michael V. Regna1, Vanessa D. Enriquez-Ríos1, Paula Mende1, Kimberly L. Turner2,4 and Heather D. Maynard1,2.

1California NanoSystems Institute, University of California Los Angeles, Los Angeles, California; 2Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California; 3Mechanical Engineering, University of California Santa Barbara, Santa Barbara, California; 4California NanoSystems Institute, University of California Santa Barbara, Santa Barbara, California.

The emerging technology of protein micro and nanoarrays offers exciting possibilities for biosensor applications due to the increased sensitivity over current clinical tests. The resolution of commercially available arrays is limited due to the robotic printing techniques that are adopted in fabrication. As an alternative approach, we recently developed a methodology for protein patterning using pH-responsive polymer films and photolithography. This technique uses poly(3,3-diethylpropyl methacrylate) (PDEMA), which contains reactive acetoxy groups that hydrolyze to aldehydes in the presence of acid. Aldehyde easily react with amines via reductive amination. We first demonstrated micro scale protein patterning (18 x 18 micron features) using PDEMA, the photoduced generator (PAG)
triphenylsulfonium triflate, and deep ultraviolet light (λmax=248 nm). In the current study, we examine the utility of PDEPM for protein patterning at the sub-micron scale. PDEPM plus phosphoglycerol diphenylglycoluril-9,10-dimethoxyanthracene-2-sulfonate (DIAS) were spin-coated onto C4F8 coated silicon wafers. Silicon wafers were treated with C4F8 gas injected into plasma in order to create a more hydrophobic and hydrophilic surface, which promotes better surface adhesion of the polymer. Samples were then exposed to I-line light using a GCA 6300 I-Line Wafer Stepper at the UCSB Nanofabrication Facility for 4 seconds through a mask. The mask contained arrays of features ranging from the micron to sub-micron scale. Topographic AFM images revealed patterned features down to 500 nm. Conversion to aldehydes resulted in a decrease in the height of the polymer film by approximately 18 nm. In order to pattern proteins at locations exposed to I-line light, samples were first stained with a biotinylated hydroxylamine (ARP) followed by red or green fluorescent streptavidin. Streptavidin binds specifically to locations of light exposure, with minimal background staining. Due to the multiple binding sites on streptavidin for biotin, biotinylated proteins may then be attached to the arrays for use in enzyme linked immunosorbent assays. Alternatively, antibodies could be functionalized with an aminooxy and directly conjugated to aldehydes on the polymer film. The I-line Stepper allows for alignment, thus multiple proteins could be patterned for the development of biosensors and protein arrays with feature sizes on the sub-micron scale.

**O9.36**

**Functionalized Nanoporous Membranes for Biocatalytic Flow-Through Reactions.** Mato Knez1, Miroslav Malesevic2, Woo Lee1, Marat B. Malesevic2, Matti Pakkanen1, Kornelius Niebsch1, Lauri Niinisto3 and Ulfir Goezele1

1 Max Planck Institute of Microstructure Physics, Halle, Germany; 2Max-Plank Research Unit for Enzymology of Protein Folding, Halle, Germany; 3Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, Helsinki, Finland.

Porous alumina membranes are well-established template systems for the synthesis of a large variety of nanostructured materials. When we introduce imprint lithography in the fabrication process of this porous structure, a monocrystalline arrangement of pore channels on a cm^2-scale is obtained and the deviation of the pore diameter is reduced to less than 2%. However, alumina membranes do not provide high compatibility for biomolecules and therefore are not suitable for biomolecular reactions. In order to achieve well-defined and biocompatible membranes, the chemical composition of the alumina template surface needs to be modified. Coating of alumina membrane surfaces with gold and titania is achieved by electrochemical methods and atomic layer deposition (ALD). Subsequently wet-chemical methods can be applied to adsorb monolayers of linker molecules which act as adhesive interfaces for binding proteins and enzymes covalently. In the case of gold membranes thiold-acted active linker molecules and for titania membranes phosphatc capped ones are used. A typical model system for the protein reaction is the well-known streptavidin–biotin system and for the enzyme catalysis the reaction of luciferase with the high surface area of this system. High yields in a one-step reaction are achieved by simply forcing the reactants to pass the membrane. The high potential of the reactors can further be enhanced by stacking of several tailor-made membranes in order to achieve multi-step reactions (e.g. for peptide synthesis). By varying the pore diameter from 10 nm to 400 nm, enzyme-catalytic reactions with small molecules as well as with large-sized ones can easily be performed. We thank the German Ministry for Education and Research (BMBF, project number 03N8701) for financial support.

**O9.37**

**N? Detection by the Carbon nanotubes Mat and Bundle.** Chien-Sheng Huang, Bohr-Ran Huang and Meng-Shian Tsai

Department and Institute of Electronic Engineering, National Yunlin University of Science and Technology, Touliu City, Yunlin, Taiwan.

Carbon nanotubes (CNTs) were synthesized by thermal chemical vapor deposition (thermal CVD) on n-type Si(100) at 700°C under CH4/H2 gas flow ratio of 30 sccm. Fe catalysts were pre-deposited by RF sputtering with RF power 150 W. Two kinds of as-grown CNTs were used to detect N2: the vertically oriented CNTs mat and horizontally oriented CNTs bundle. Two-terminal electrical measurements were performed at a room temperature of 25°C. The electrical resistance of CNTs mat and bundle was found to increase as which exposed to N2 environment, and to return back after the N2 pumping, respectively. However, the CNTs bundle had better sensitivity and possessed faster response and recovery time. This could be attributed to that the CNTs bundle has more effective grooves on the surface, provided more lower binding-force bind sites to absorb N2 molecules than the CNTs mat, which prominently has interstitial sites. A three-terminal electrical measurement would be further performed to clarify the characteristics of N2 absorption under different applied gate voltages.

**O9.38**

**Nanoforest-linked amperometric immunosensors with nanomolar detection limit.** Sang Kyung Kim1, Xin Yu2, Fotion Papadimitrakopoulos1,2 and James F. Rusling1


Amperometric enzyme-linked immunosassays were developed based on vertically aligned arrays of single-wall carbon nanotubes (SWNTs) coated on pyrolytic graphite electrode surfaces. SWNTs have high surface coverage and low amount of defects enhanced biorecognition performance (3.5-fold sensitivity improvement), which was monitored by using nanotube-bound peroxidase enzymes. Mediator-free detection of H2O2 indicated an efficient electron exchange between the nanotubes and the enzymes attached to their ends. Sandwiched protein immunosensors were fabricated by attaching antibodies to the carbohydrate end of nanotube forests. Non-specific binding was minimized by utilizing casin/detergent and a detection limit of 75 pmol/l. The achievement of human serum albumin (HSA) was achieved by unmediated sandwich immunosassaying using horseradish peroxidase (HRP) labels. Much lower detection limit (c.a. 1 pmol/l) was acquired by using hydrogen peroxide, as a mediator, providing significantly better performance than alternative media. I. Chattopadhyay, D.; Galeska, I.; Papadimitrakopoulos, F.; Metal-Assisted Organization of Shortened Carbon Nanotubes in Monolayer and Multilayer Forest Assemblies. Journal of the American Chemical Society 2001, 123, (24), 6451-6452, 2000, 9451-9452, 2001, 97, 813-820, 1993, 105, 2, 436-442, 1982, 104, 6, 1619-1632, 1982, 104, 6, 1619-1632, 1982, 104, 6, 1619-1632, 1982, 104, 6, 1619-1632, 1982. Papadimitrakopoulos, F.; Rusling, J. F., Protein immunosensor using single-wall carbon nanotube forests with electrochemical detection of enzyme labels. Molecular BioSystems 2005, (1), 70-78.

**O9.39**

**The Use of Magnetron Sputtering for the Preparation of Catalytic Gold Nanoparticles.** Gabriel Mark Veih1, Andrew R. Lupini1, Sergey N. Rashkov2, Stephen J. Fenyoeook and Nancy J. Dudney

Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

This presentation will describe a new truly one-step technique to prepare catalytically active gold nanoparticles on a variety of supports. The method involves magnetron sputtering of a high purity metal target and the subsequent deposition of the metal onto a catalyst support. This method allows us to prepare catalysts that are not accessible using classic chemical preparation techniques or are only possible using complex preparation methods. Examples include catalytically active 2 nm gold nanoparticles on SiO2 and gold on various forms of carbon. Additional supports will also be discussed along with their activity towards selective oxidation reactions. Specific emphasis will be placed on the correlation between experimental results, aberration corrected STEM microscopy and theoretical calculations. Acknowledgement: This work was supported by the US DOE’s Division of Materials Science under contract DE-AC05-00OR22725 managed by UT Battelle, LLC.

**O9.40**

**Localised Heating of Magnetic Nanoparticles for Biological Control.** Andy Wijaya1 and Kimberly Hammad-Schifferli2

1 Chemical Engineering, MIT, Cambridge, Massachusetts; 2Biological Engineering, MIT, Cambridge, Massachusetts.

The use of magnetic particles under AC magnetic field as localized heating sources for biological applications has been extensively investigated for hyperthermia in the past couple of decades. Not until recently (Hammad-Schifferli, K., et al. Nature, 415, 152-155 (2002)) has this technique been applied on the molecular level to control the dehybridization of DNA molecules. Consequently, this technique shows potential to be utilized as a tool for the study of biological systems. However, as most biological processes involve multiple species, we need to show that this technique can be applicable to multiple nanoparticles. We explore the heating rates of magnetic nanoparticles of different materials and sizes (d = 3-10nm) under the influence of an AC magnetic field. These studies would lead to the development of multiple magnetic nanocrystal antennas to control multiple biomolecules independently.

SESSION O10: Catalysis III

Chairs: Valeri Petrov and Chun-Jiang Zhong

Thursday Morning, December 1, 2005
Room 201 (Hyatt)

8:15 AM O10.1

**Synthesis of Nanocrystalline N-Doped TiO2 for Photocatalytic Applications.** Kranthi Kumar Makari1,2

1,2
Vital1, Thomas Graule1 and Markus Winterer;1 1High Performance Ceramics, EMPA, Swiss Federal Laboratories for Materials Testing and Research, Zuerich, Switzerland; 2Process Technology, Department of Engineering Sciences, University Duisburg-Essen, Duisburg, Duisburg, Germany.

Since photoinduced decomposition of water on TiO2 electrodes was discovered, semiconductor based photocatalysts has attracted extensive interest. TiO2 combines good electrical properties with high catalytic activity and excellent stability in many solvents over a wide range of pH. Because of the band gap, TiO2 is not absorb visible light which is a large part of the solar spectrum. So, any shift in the optical response of TiO2 from the UV to the visible spectral range will have a profound positive effect on the photocatalytic activity of the material. This can be obtained by narrowing the band gap. By using anionic (C, N, F, P and S) dopant species band gap narrowing can be achieved. Here we report the synthesis of nitrogen-doped TiO2 by feeding TiCl4 precursor along with NH3 gas and air through a hot wall reactor. The flow rates of the ammonia gas and air are optimised to achieve a desired amount of nitrogen doping and the size of the particles is controlled by varying TiCl4 precursor concentration and the temperature of the hot wall reactor. Particles are collected on the filters by using a vacuum pump at the exit of the hot wall reactor. A schematic particle formation mechanism is proposed and the significance of using TiCl4 as the precursor source is discussed in detail. Resultant particles are characterized by BET surface area analysis, XRD, TEM, XPS and UV-Vis spectroscopy. Conclusive evidence is obtained for Ti-O-N bond formation by XPS measurements. The nitrogen doping causes the absorption of TiO2 to be shifted to the long wavelength region and the color of the powders is blue which is used as the model pollutant to study the photocatalytic activity of these powders. Increase in the photocatalytic activity in the visible light region is correlated to the doping of nitrogen and concurrent reduction in the band gap.

8:30 AM *Q10.2 Shape-Dependent Nanocatalysis and the Effect of Catalysis on the Nanoparticle Shape and Size in Colloidal Solution.
Mostafa A. El-Sayed and Radha Narayanan; School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia.

This talk will discuss our results on nanocatalysis in colloidal solution of two reactions, a mild electron transfer reaction and a harsh Suzuki carbon-carbon coupling reaction. There is definitely shape dependence of the activation energy of these reactions, and the nanoparticles with larger fraction of its atoms present at the edges and on corners are found to have the lowest activation energy. We also found that the activation energy increases during the reaction as a result of the shape changes which tend to round out the edges and the corners.


9:00 AM *Q10.3 Tuning of Nanocrystalline Catalytic Structures for Microreactor Applications, Hailbing Chen and Woo Y. Lee; Chemical, Biomedical, and Materials Engineering, Stevens Institute of Technology, Hoboken, New Jersey.

Microcrystalline structures of silica were synthesized in microchannel reactors using silica nanoparticles and polymer microsphere templating methods in the cell size range of 10 to 20 micrometers. This type of structure, if uniformly coated with a thin-film catalyst layer, is expected to provide several desired attributes (i.e., low pressure drop, improved mixing, and low mass transfer resistance) for improving microreactor performance particularly for reactions involving a liquid phase. For our synthesis method developed, polystyrene microspheres were packed into the microchannel from suspension, and the silica nanoparticles were infiltrated into the interstices of the microsphere template. After drying and sintering, the solid silica and the microspheres were removed to create interconnected cells defined by the silica skeleton structure. The structure and properties of the microcrystalline silica were tuned by systematically controlling three key parameters: cell size, cell interconnectivity, and skeleton porosity. "Nanocatalysts", filled with the microcrystalline catalytic structures were used to carry out hydrogen peroxide synthesis, and were compared with packed-bed microreactors.


Ceria-zirconia-based systems are promising as components of three-way-catalysts, catalysts of selective oxidation/autothermal reforming of hydrocarbon fuels to form high-temperature fuels for solid oxide fuel cells. Doping this system with valence cations allows to stabilize this solid solution in hydrothermal conditions and tailors the lattice oxygen vacancies depending on the defect concentration and gas composition. In this work, nanocrystalline samples of Pr/Gdx(1-x)/ZrO2 (x=0.1, 0.2, 0.3) were studied by x-ray Diffractometry, IR spectroscopy of lattice modes and adsorbed CO and NO, CH4 and H2 TPR. Pr was supported on a impregnation method. Catalytic properties of Pt-loaded samples were studied in the reaction of methane selective oxidation into syngas at short contact times. All samples are found to be single-phase nanocrystalline systems of a cubic fluorite-like structure. With increasing the dopant content, the unit cell increases, while the size of domains decreases from 6 to 3.5 nm. This suggests that dopants are in part segregated at domain boundaries preventing their sintering. Appearance of complex defects within domains is reflected in their disordering as revealed by EXAFS, IRS of lattice modes and Raman spectroscopy. A higher degree of Pt cations segregation is reflected in the positive deviation in the dependence of the lattice parameter on x from the linear trend at x=0.3. According to the data of IR spectroscopy of adsorbed CO and NO, for both doped systems the concentration of surface coordinatively unsaturated cations passes through the minimum at x=0.3. This is reflected in the minimum of the middle-temperature lattice oxygen mobility at this dopant content as revealed by CH4 and H2 TPR data. Hence, incorporation of dopants into the lattice of ceria-zirconia solid solution generates more simple defects than simple vacancies, since the vacancies concentration is expected to increase at a low doping level. A higher lattice oxygen mobility at a high dopant content suggests a fast oxygen transport along disordered domain boundaries and extended defects. Pt supported on Ce-Zr doped oxides results in pronounced interaction between the metal and support, which is reflected in stabilization of Pt ionic forms in part incorporated into domain boundaries, leading to their further disordering. This is reflected in variation of the bulk oxygen mobility which now reaches a minimum at a lower (x=0.1) dopant content as revealed by TPR experiments. Similarly, specific catalytic activity in the reaction of methane selective oxidation into syngas by molecular oxygen also goes through the minimum at the same dopant content. Pt-supported Pr-doped oxides are more active than Gd-doped samples. This work is in part supported by ISTC 2529 and NATO SFP 090878 Projects.

9:30 AM *Q10.5 Practical nanomaterials and nanoarchitectures in electronics.

A quiet revolution is occurring in electronics where nanomaterials have the ability to revolutionize adhesives and solders, nano oxides are revolutionizing fuel cell efficiency, and nanowires as well as nanoribbons have the potential both to enhance short term evolutionary and long term revolutionary improvement. This paper outlines some roadmap predictions and picks three areas with concrete examples- nano metals for ink jet formation of circuits, nano oxides in fuel cells, and lithographically developed nanowires for sensor application and details technical and commercial progress.


Nanostructured TiO2 based ceramics were synthesized using citrate-nitrate auto combustion method with different concentrations of aluminum oxide as dopant. The powder x-ray diffraction data showed that the synthesized TiO2 powders, prior to calcination at 550°C, had anatase phase. Doping concentration varied between 5 and 15 wt%. Particle size analysis showed below 100nm particles for pure TiO2 as well as doped TiO2 samples. Average particle size of doped powders was generally lower than pure TiO2. The BET specific surface area analysis showed change in specific average surface area with increasing dopant concentration, and different synthesis and processing parameters. BET specific average surface area was between 45 and 50 m2/g. Using pressed compacts using these nanopowders showed an increase in
oxidation. Copper-based catalysts are used in a number of industrial processes involving metal production, methanol reforming to produce hydrogen, or methanol partial oxidation to synthesize formaldehyde. Oxygen on Cu surfaces is known to activate activity for methanol decomposition, but the possible effects of nanometer-sized Cu2O surface islands on the induced surface behavior are not understood, primarily because of the scarcity of atomic-scale structural and chemical information obtained under reaction conditions. We are employing novel in-situ x-ray techniques to characterize methanol oxidation on Cu (001). A quartz-walled deposition system that allows controlled mixtures of oxygen, methanol vapor, and other gases to be flowed at conditions from atmospheric pressure to 10\(^{-2}\) Torr has been specially constructed to mount onto a six-circle diffractometer at the Advanced Photon Source. Reaction products are monitored with a residual gas analyzer, and a substrate heater allows reactions to be carried out at temperatures from 250 to 1600 °C. We observe that exposure of the clean Cu surface to low controlled partial pressures of oxygen (P(O2) \(\approx\) 10\(^{-5}\) Torr) results in the formation of either a c(2x2) or a (2sqrt2x2sqrt2)R45° surface reconstruction, depending on temperature. With increasing pO2, Cu2O nano-islands nucleate and grow. We observe that the equilibrium phase boundary between CuO and c(2x2)-Cu2O nanoflakes in shadowed areas is shifted to several orders-of-magnitude larger oxygen partial pressures than predicted by bulk thermodynamics. The effects of methanol exposure on surface structure and oxide island stability will be described in this presentation. Initial results on the structure and on the catalytic activity for methanol oxidation will also be discussed.

10:45 AM Q10.8

One-pot synthesis of mixed ionic-electronic conducting nanocomposites comprised of fluorite-like and perovskite-like phases as catalytic materials for SOFC. Vladislav A. Sadykov\(^1\), Yulia V. Frolova\(^2\), G. M. Aliksina\(^2\), A. I. Lukashiev\(^1\), R. V. Bunina\(^1\), E. M. Moroz\(^2\), V. A. Rogov\(^1\), V. I. Zaikovskii\(^1\), A. V. Ishchenko\(^1\), V. K. Kriventsov\(^2\) and N. Orlovskaya\(^3\); \(^1\)Borsec Institute of Catalysis, Novosibirsk, Russian Federation; \(^2\)Drexel University, Philadelphia, Pennsylvania.

Nanocomposites comprised of ionic (doped ceria) and electronic conductors are considered as a promising option for design of catalytically active cathodes and/or anodes in SOFC, membranes for oxygen and hydrogen gas separation. Ball-milling of the mixture of coarse powders of constituting phases is a traditional approach in the synthesis of composites leading to a poor percolation. This work presents results of research aimed at one-pot synthesis of nanocomposites consisting of ceria and rare-earth manganites phases. The approach is based on the modification of polymerized precursor (Pechini) route with fixing all constituting cations in the citric acid-ethylene glycol polymer matrix followed by its burning and calcination. Due to a limited solubility of Mn and La cations in ceria as well as Ce in the perovskite lattice, perovskite-fluorite nanocomposite is expected to be formed directly at calcinations provided chemical composition of the system is properly chosen. Along with ternary GDC + Gd-Mn-O system (perovskite-fluorite ratio \(\approx\)1:1), an industrial mixture of La, Ce, Pr, Nd, Sm salts was combined with Mn nitrate in a ratio required to produce perovskite-fluorite 1:1 nanocomposite. The synthesis of the phase composition and the phase structure of these complex systems was followed by HRTEM with EDX, XRD, and Raman. After calcinations at 500 °C, only nanocrystalline metastable fluorite-like phase is observed. Excessive dissolution of doping elements in the perovskite lattice is also observed by inductively coupled plasma analysis. Cell size. Some spatial variation of the elements distribution between domains is revealed by EDX. This agrees with observed Raman bands at \(\approx\)220, \(\approx\)480 and \(\approx\)850 cm\(^{-1}\) suggesting presence of fragments with both fluorite-like and perovskite-like structures. Air annealing at temperatures exceeding 800 °C results in segregation of nanocrystalline perovskite-like phase. Domain sizes of both phases remain in the nano-range up to 1100 °C. Strong coordination of Ce-Me and Mn-Me coordination decreases upon formation of the fluorite phase. Air annealing above the perovskite-like phase also results in a decrease in the lattice oxygen mobility and reactivity estimated by O\(_2\) uptake TPD, H\(_2\) and CH\(_4\) TPR increase with temperature of nanocomposites exhibiting due to homogeneous perovskite on the surface. It is confirmed by a high electronic and ionic conductivity measured for nanocomposites.

sintered pellets. A high rate of methane and decane combustion in the 600-800 °C temperature range by the lattice oxygen of nanocomposites could be expected as a mixture of fluorite and perovskite phases. The reaction rates as direct oxidation anodes in SOFC. These systems were also found to possess a high activity and selectivity in the reaction of hydrocarbons selective oxidation and autothermal reforming into syngas at short contact times, while being stable to coking. This research is in part supported by SFP Project 980878 and ISTC.

11:00 AM Q10.9


Anodized aluminum oxide (AAO) membranes consist of highly uniform and aligned nanopores with the pore diameter ranging between 10 and 200 nm. Based on these nanoporous materials, we have developed a new AAO nanowell structure that was synthesized through a short-term anodization on surfaces. The nanowell structure is made of shallow wells that were oriented in a hexagonally closed packing configuration with well diameter around 50 nm and depth less than 100 nm. The chemical composition is amorphous alumina on aluminum substrate. Thin palladium film was then fabricated on the surface of the as-synthesized AAO nanowell to prepare a Pd/AAO nanowell structure. These devices show unexpectedly high hydrogen sensing capability. The response time ranges between a few hundred milliseconds and a few seconds at hydrogen concentration between 2 and 0.05%. They also show modest responses at hydrogen concentration as low as 5 ppm. The morphology of these Pd/AAO nanostructures and their sensing mechanism will be discussed at Argonne National Laboratory as well as measurements with FESEM carried out at EME at ANL are supported by USDOE, the office of Basic Energy Sciences, Division of Materials Science under Contract # W-31-109-Eng-38.

11:15 AM Q10.10

The Electrosynthesis and Evaluation of WO\(_3\) Nanowires for Chemical Microsensor Applications. Kurt D. Borchstein and Steve Senumack; CSTL, Institute of Standards and Technology, Gaithersburg, Maryland.

Nanowires have been attracting significant interest in nanoelectronic applications, such as optical devices and chemical sensing. Because we utilize temperature changes to vary interfacial interactions in our chemical microsensors, we have a particular interest in elucidating the effect of the operating temperature and the morphology of the active nanomaterials on response characteristics. Nanowires composed of WO\(_3\) (a material particularly responsive to NO\(_2\) compounds) are being developed to examine effects of temperature control on wire functionality for analyte detection. We describe in this presentation the results on WO\(_3\) nanowire fabrication as well as on their efficacy as the active material in conductometric chemical microsensors. Production of WO\(_3\) nanowires was achieved via template-directed electrosynthesis from solutions of W\(_2\)O\(_7\)\(^{2-}\) in track-etched polycarbonate membranes (\(d_{core} = 100\) nm). The nanowires were characterized by optical and scanning electron microscopies, which showed that the nanowires were \(\approx 2.5 \mu m\) long and varied from 125 nm to 175 nm in diameter. Initial studies of the performance of the nanowires as the active material in conductometric chemical microsensors were performed on multiple wires deposited over interdigitated electrodes on MEMS microhotplate platforms. These platforms allow temperature-dependent behavior properties and response characteristics to be rapidly measured between 20 °C and 480 °C. Comparisons were made between the nanowires and WO\(_3\) particulate films prepared by calcination of H\(_2\)WO\(_4\). Both types of WO\(_3\) films were evaluated as conductometric sensor materials for several target analytes, including NO\(_2\) and methanol, in air-based background environments.

11:30 AM Q10.11

Fabrication and electrical characterization of gas sensors based on tailored, tin oxide nano-particle. Tim Patrick Huesler\(^1\), Pascal Heacho\(^2\), Hartmut Wiggers\(^2\) and Axel Lommatzsch\(^1\); \(^1\)University of Duisburg-Essen, Duisburg, Germany; \(^2\)Institute of combustion and gas dynamics, University Duisburg-Essen, Duisburg, Germany.

 Rutile tin oxide (SnO\(_2\)) nano-particles with mean diameter of 7 nm were synthesized in a low-pressure, H\(_2/O_2/Ar\) premixed flame, doped with tetramethyltin. The synthesized tin oxide nano-particles were deposited from a particle laden molecular beam on an inter-digital capacitor. The inter-digital capacitor was fabricated on a P versatile silicon oxide substrate using electron beam lithography. They consist of gold fingers with distances and widths, that were varied from 200 nm to 2000 nm to optimize the sensing behaviour. Using impedance spectroscopy, the AC-conductivity of the nano-particles was investigated under N\(_2\) atmosphere and as well as under synthetic air.
in the temperature range between 323 K and 503 K. For particles on inter-digitizer capacitors with a distance and width of 1 micron, two different causes to the overall impedance were determined under N₂ atmosphere. Changing the atmosphere to synthetic air, an additional contribution to the overall impedance was resolved in the lower temperature range. From a comparison with the response under N₂ atmosphere, this contribution is attributed to the presence of oxygen in the synthetic air. By fitting the measured data with an equivalent circuit, consisting of a series of an ohmic resistor R and parallel RC elements, these contributions could be assigned to bulk resistance, intergranular contacts and electrode-particle contacts. As expected for a semiconducting material, the resistance decreases exponentially with increasing temperature. To gain more insight into the relevant transport mechanisms, activation energies of the different contributions were determined from Arrhenius plots. Of the findings, particularly the additional detectable transport mechanism under oxidizing atmosphere open new routes for low temperature oxygen-sensing devices based on tin oxide nanoparticles.

SESSION O11: Sensor and Biosensor
Chair: Chuan-Jian Zhong and Shuqin Zhou
Thursday Afternoon, December 1, 2005
Room 200 (Hynes)

1:30 PM O11.1
1Mechanical & Materials Eng., Wright State University, Dayton, Ohio; 2Materials & Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio.

Raman spectroscopy is a technique that probes materials on the molecular level by monitoring inherent vibrational modes. The technique has been successfully utilized to investigate material systems on the micro and the nano-scales and more recently has proven its ability to exploring systems on the nano-scale. For example, detailed analysis of the Raman spectrum of a carbon nanotubes provides important information regarding the nanotube diameter, chirality, and conductive properties. In this talk, our recent work regarding the ability of single-walled carbon nanotubes and carbon C60 nanoparticles to sense their chemical environment will be discussed. Experimental results will be compared to the predictions of quantum mechanics calculations. The current findings represent a major new thrust for the development of new nanostructured chemical and biological sensors.

1:45 PM O11.2

For intracellular sensing is highly desirable to form small (nanometer-scale), long (micrometer-scale), strong, and electronically active bio-chips. Such probing needles are challenging to fabricate by traditional methods. Moreover, for most applications, these nano-noodles need to be mechanically anchored in and electrically interfaced with a solid micro (or macro) base. For the ease of charge transfer, a solid base is preferably to be silicon. Furthermore, for intracellular probing and explorations, these probing nano-noodles should be vertically aligned and parallel to each other, uniform in height and diameter, and densely spaced in an array form. All these demands are generally hard to meet in micro or nano-fabrications. Yet, for the technology to be viable, the fabrication method to be developed must be kept simple, scalable and low-cost. In this work, we report a success we made in fabricating highly-ordered and densely-spaced array of nano-noodles that appear to have met most, if not all, of the challenging demands and that are fabricated with a relatively simple and non-lithographic method. An array of densely-spaced nano-noodles of high uniformity in length and diameter are created in silicon in this approach by reactive ion etching (RIE) through an array of metallic nano-dot caps that are evaporated on a silicon wafer through an anodic aluminum oxide (AAO) membrane. The AAO membrane with highly-ordered and highly-uniform nano-pores is formed non-lithographically via anodization of pure aluminum foil. The particular AAO membrane used in this demonstration experiment is one that is chosen to have pore diameter, pore spacing, and membrane thickness of ~50nm, ~100nm and ~500nm, respectively. We found that by keeping the AAO membrane extremely thin, uniform metallic nano-dots can be e-beam evaporated through the nano-pores on a planar silicon surface, and are adhesive and strong enough to sustain the subsequent RIE process through the formation of the desired array of silicon nano-noodles of ~30nm in diameter and ~4nm in length.

2:00 PM O11.3

Dendrimer-encapsulated nanoparticles (DENs) of easily oxidizable metals were prepared using hydrophobic dendrimers. These materials were best prepared under non-aqueous and anaerobic conditions, and therefore a toluene-based synthesis was employed. Specifically, a G6 PAMAM hydrophobic dendrimer consisting of a metal precursor were dissolved in toluene. This resulted in the formation of a metal-ion/dendrimer complex after 10 min. Subsequent reduction yielded nanoparticles with <150 metal atoms per dendrimer. Monometallic DENs consisting of Co, Cu, Fe, and containing 147 and 55 atoms were prepared. The resulting materials were nearly monodisperse in size (< ±0.3 nm). The magnetic properties of these DENs were measured using a superconducting quantum interference device (SQUID). The materials demonstrated superparamagnetic behavior. All DENs studied possessed hysteresis-free magnetism at temperatures of 5.0 K. The saturation values, from hysteresis studies, demonstrated an increase dependence upon the particle size. This analysis correlated well with previous studies indicating analogous magnetic saturation effects from larger nanoparticles of similar compositions.

2:30 PM O11.4
A Regenerative Biosensor of Hydrogen Peroxide Based on Rare Earth Oxide Nanomaterial, Swapna D. Patil 1, 2, Anjum Mehta 1, Hyoungseok Bang 1, Hyoun J. Cho 3 and Sudipta Seal 1. 1Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida; 2Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida; 3Department of Electrical Engineering, University of Central Florida, Orlando, Florida; 4Creol, College of Optics and Photonics, University of Central Florida, Orlando, Florida.

Hydrogen peroxide (H₂O₂) is not only the product of the reactions catalyzed by a large number of highly selective oxidases but also an essential mediator in food, pharmaceutical and environmental analysis. Its determination plays an important role in chemical, biological, clinical and many other fields. In this work, the development of a novel cerium oxide nanomaterial based electrochemical sensor for the measurement of hydrogen peroxide is described. This has direct ramifications in the development of sensors for other superoxide radicals. Cerium oxide nanoparticles were synthesized using microemulsion method to obtain uniform nanoparticle size of 3-5nm with no agglomeration. A terminal amperometric sensor was designed for the hydrogen peroxide measurement. It consists of a cerium oxide covered working electrode, an Ag/AgCl reference electrode and a gold counter electrode on a glass substrate. Nanoceria sol was deposited and dried at 150 degree C on the working electrode. Electroplating followed by chlorination formed the Ag/AgCl reference electrode. The sensor was characterized using cyclic voltammetry to obtain the working potential. Flow of hydroxyl ions was measured for varying concentrations of the hydrogen peroxide (H₂O₂) solution. A direct co-relation between the sensor signal and the (H₂O₂) concentration was observed. X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of both, Ce³⁺ and Ce⁴⁺, ions in the synthesized nanocrystalline cerium oxide. This mixed oxidation state in the nanocrystalline ceria is a key for its regenerative sensor property. Hydrogen peroxide generates free radicals which can be scavenged by cerium oxide nanoparticles via surface chemical reactions to change its valence from Ce³⁺ to Ce⁴⁺. Due to various surface chemical reactions the nanocrystalline ceria goes back to Ce³⁺ oxidation state. These ongoing reactions in opposing directions ensure continuous regeneration of Ce³⁺ ions, which aids in the longevity of the sensor. Compared to the previously developed H₂O₂ sensors, nanocrystalline cerium oxide’s regenerative property (Ce³⁺ → Ce⁴⁺ → Ce³⁺) makes it a very attractive proposition as the sensor lifetime is significantly increased.

3:00 PM O11.5
Effects of Materials Chemistry on Conductometric Sensor Signals. Douglas C. Meier and Steve Semancik; Process Sensing Group, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland.

Absorbed molecules can chemically interact with certain types of substrates to cause changes in the electrical conductivity of the material. Observation of such changes is the basis of operation of the conductometric class of chemical sensors. MEMS chemical sensors developed at NIST not only take advantage of the enhanced response capabilities of microscale (100 μm) technology, but also benefit from the rich complexity of target analyte interactions with nanoparticle (<200 nm) metal oxide substrates. These interactions and the electrical properties that arise from them are based upon the identity
of the analyte molecule, the operating temperature of the sensor device, and the physical and chemical properties of the sensing film. In this study, we have thermally addressed, temperature-controlled (to 500 °C) microsensor array elements are used to explore the performance in real time of a variety of candidate sensor materials produced by thermally activated, self-lithographic chemical vapor deposition (CVD). Microsensor array Ni/SnO2 work well focused upon the detection properties of SnO2 or TiO2 nanoparticle thin films produced by single-source CVD. The chemical and electronic differences between these oxides make them a complimentary pair for a number of applications. SnO2 film grown on a single-crystal anhydrous nitrate precursor exhibit higher overall conductance and better dynamic range for detection of alcohols, while TiO2 grown from titanium tetraiodide (TTIP) demonstrates higher sensitivity to low vapors. We have expanded upon the chemical performance orthogonality of this pair of oxides via simultaneous and layer-by-layer co-deposition of stannia and titania, ruthenium doped of oxide films via co-deposition of triruthenium dodecacarbonyl, and diiodide and TiO2 from other precursors. From film conductance measurements in organic analytes and water vapor, we demonstrate that layered oxide films generate signals that are distinct from that of either oxide. Furthermore, inclusion of ruthenium in titania films changes the time- and exposure-dependent conductance signal for certain analytes, suggesting that both chemical effects and physical effects play important roles. Materials- and process-dependent grain size and morphology are probed using scanning electron microscopy (SEM); these physical properties, as well as stoichiometry, are correlated to sensor performance. We further demonstrate that this materials-dependent response orthogonality can be used to tune the sensor temperature-dependent sensor responses as a basis for tunable analyte identification. Using this approach results in greater analyze selectivity in devices based upon analyte adsorption and substrate interaction mechanisms that are for most purposes considered non-selective.


We have investigated the use of nanowires bridging microfabricated electrodes as a kind of bioelectronic switch. Dielectrophoretic manipulation combined with a small fluid flow provides a way to manipulate nanowires into the junctions, where DC fields and biological interactions can be used to bind them in place. Using an optical microscope, it is possible to directly observe the manipulation of individual Si and Au nanowires with diameters as small as 40 nanometers. We use a combination of high-frequency AC manipulation and low-frequency detection methods to examine the changes in electrical response that accompany nanowire bridging, and measure simultaneous real-time video images to confirm that origin of the electrical signals. We have also applied this method to manipulate and detect individual bacterial cells that are ~3 microns long and ~750 nm in diameter, which are slightly larger than many nanowires of interest. Measurements on nanowires show that the electrical response includes contributions from the capacitance associate with the electrical double-layer, as well as the solution resistance. In this talk we will discuss the dielectrophoretic manipulation of nanowires and our recent work measuring the changes in electrical response in real time.

3:45 PM **O11.7** Development of Biofunctional Magnetic Nanoparticles for Pathogen Detection and Anticancer Therapy. Jinhao Gao1, Zhihong Yang1, Keming Xu1, Hongwei Gu1 and Bing Xu2.

1Chemistry, The Hong Kong University of Science and Technology, Hong Kong, NA, Hong Kong 2Biomedical Program, The Hong Kong University of Science and Technology, Hong Kong, Hong Kong.

This talk will focus on the development of biofunctional nanomaterials based on magnetic nanoparticles. We will demonstrate that the integration of fluorescence and magnetic nanoparticles for ultra-sensitive pathogen detections. Compared to conventional used magnetic particles in the sizes of 1-5 μm for drug delivery, magnetic nanoparticles, combining with fluorescent-labeled receptor-ligand interactions, provide a ultra-sensitive and rapid protocol to detect pathogens. In addition, this talk will also discuss the surface chemistry of the synthesis of novel nanostructures (e.g., porphyrin decorated iron oxide nanoparticles) and their application as an anticancer agent in both photodynamic therapy (PDT) and hyperthermia treatment (HT).

4:00 PM **O11.8** Highly Selective Sensing of Nerve Agents Using Nanostructured Ultrathin Films of Electrochemically Oxidized Pyrrole. Rigoberto Advincula and Prasad Taranekar; Department of Chemistry, University of Houston, Houston, Texas.

Over the past two decades, the research and development of chemical sensors has been of prime interest for applications ranging from separations to remote sensing. For chemical warfare and terrorism defense, there is a continuous need for new and improved methods for the detection of nerve agents. The combination of high sensitivity and selectivity in sensor design is a major challenge. Towards this end, we have utilized two strategies: (i) the use of fluorinated polymer layers for the fabrication of ultrathin sensor films and (ii) the use of specific functional groups to enhance the selectivity of the sensor films. Our work has been focused upon the detection of SnO2 or TiO2 nanoparticle thin films produced by single-source CVD. The chemical and electronic differences between these oxides make them a complimentary pair for a number of applications. SnO2 film grown on a single-crystal anhydrous nitrate precursor exhibit higher overall conductance and better dynamic range for detection of alcohols, while TiO2 grown from titanium tetraiodide (TTIP) demonstrates higher sensitivity to low vapors. We have expanded upon the chemical performance orthogonality of this pair of oxides via simultaneous and layer-by-layer co-deposition of stannia and titania, ruthenium doped of oxide films via co-deposition of triruthenium dodecacarbonyl, and diiodide and TiO2 from other precursors. From film conductance measurements in organic analytes and water vapor, we demonstrate that layered oxide films generate signals that are distinct from that of either oxide. Furthermore, inclusion of ruthenium in titania films changes the time- and exposure-dependent conductance signal for certain analytes, suggesting that both chemical effects and physical effects play important roles. Materials- and process-dependent grain size and morphology are probed using scanning electron microscopy (SEM); these physical properties, as well as stoichiometry, are correlated to sensor performance. We further demonstrate that this materials-dependent response orthogonality can be used to tune the sensor temperature-dependent sensor responses as a basis for tunable analyte identification. Using this approach results in greater analyte selectivity in devices based upon analyte adsorption and substrate interaction mechanisms that are for most purposes considered non-selective.

4:15 PM **O11.9** Integration of Nanoparticles Into and Onto Optical Fiber Sensors. Anuj Dhawan and John Muth; ECE Dept., North Carolina State University, Raleigh, North Carolina.

The use of plasmon resonance of metallic nanoparticles for sensing is well known and has been used extensively on planar substrates for sensing applications. In this study, novel techniques of integrating optical nanoparticles into and onto silica optical fibers are discussed. A study for the islanding and formation of gold nanoparticles was performed by depositing thin films gold by e-beam evaporation on planar substrates and post annealing at temperatures ranging between 200 °C and 400 °C for short durations. The resulting nanoparticles were characterized by optical transmission spectroscopy in a variety of liquids with known refractive indices to observe the resonance shifts. The films were then characterized by AFM and SEM. With this reference data, similar nanoparticle structures were generated by coating metals on the end of optical fibers, coating the metallic layer with glass by pulsed electron beam deposition, and fusing the resulting structure to another optical fiber. This formed a compact system with to perform spectroscopy of nanoparticles. Alternative optical fiber structures with which to observe nanoparticle interactions with the environment including optical fiber tapers, and in-line coreless optical fiber structures were also investigated.

4:30 PM **O11.10** Photonic Sensors Based on Nanoparticle Sensing Chemistry. Nile Hartman, Bernard Schneider and Todd Polley; Electronics & Optics, nGimat Co., Atlanta, Georgia.

nGimat is developing an integrated optic chip (IOC) sensor platform that offers real-time, multi-agent sensing capabilities for chemical and biological agents. This technology eliminates the requirements for wet chemistry techniques and complex instrumentation common to many sensor technologies. As a result, the nGimat IOC sensor is well suited for field use by non-technical personnel or for operation as an unmanned sensor. Currently, nGimat is pursuing the use of coated nanoparticles to increase the detection sensitivity and specificity of the IOC sensor technology. The IOC sensing mechanism is based on the interferometric detection of a refractive index change occurring on the surface of the waveguide due to absorption or a reversible chemical reaction. The latter is the preferred mechanism due to the large effective index change that can occur. Nanoparticles have the potential to dramatically enhance this effect. In the current application, nGimat takes advantage of these properties by tailoring transition metal coated nanoparticles consisting of a silica core and a metal shell that is reactive with specific chemicals. Thus, so, the detection of toxic industrial chemicals. Specifically nGimat has shown that silica particles coated with copper and embedded in a polymeric matrix can easily detect hydrogen sulfide gas at concentrations in the low ppb range. For applications based on the IOC chip technology, nanoparticles offer several significant advantages. They permit the use of sensing chemistries that would normally be too lossy for the IOC approach. Generally, detecting copper metal directly on an IOC waveguide would result in extremely high losses. However, when dispersed in a polymer matrix, the losses can be avoided and the entire depth of the evanescent optical wave can be utilized. Secondly, reactive coating material can be designed that offer large relative index changes when reacted. In the case of copper, the real part of the refractive index is 0.4, but after reaction with H2S, that index changes to approximately 1.04. In the future, nGimat also plans even more dramatic enhancements through the use of nanoparticles tailored to specific sizes.
O12.1 Self-signaling amplifying bio-/synthetic hybrid sensory polymers for fast DNA detection. Kangwon Lee1, Jae Cheol Cho1, Ching-Chin Pun2, Jean Marie Roulillard2, Erdogan Gulari2 and Jinsang Kim1,2,3.

1Materials science and engineering, University of Michigan, Ann Arbor, Michigan; 2Chemical engineering, University of Michigan, Ann Arbor, Michigan; 3Biomedical engineering, University of Michigan, Ann Arbor, Michigan.

Low cost, reliable detection of bio-threat agents remains a significant challenge especially given the diversity of the potential agents which can be used for this purpose. The most reliable way of identifying the identity of any virus or microbe is through its genetic code. However, Traditional DNA detection requires amplification through polymerase chain reaction (PCR), labeling with fluorescent dyes, and thorough purifications of analyte DNA. This costly and time-consuming process makes current DNA sensors not suitable for the real-time organism detection required for bio-threat monitoring. We have been developing conjugated polymer-based bio-/synthetic hybrid sensory polymers for fast DNA detection that will provide high sensitivity, high selectivity, low false signal, self-reporting capability, and easy fabrication without the PCR amplification process labeling of analyte DNA. The long term application of the proposed technology could be the development of a self-sustained field device for bio-threat monitoring and diagnostic screening of gene-related diseases. Our bio-/synthetic hybrid sensory polymers have a conjugated amide backbone for signal amplification and side chains of oligonucleotides as receptors. Oxadiazole- alternating conjugated polymers and poly(p-phenyleneethynylene)s are the conjugated backbone. Linear oligonucleotides and hairpin-type molecular bonds are the receptor groups. Two different microarray approaches as well as solution study will be discussed. Molecular design principles for turn-on and fluorescence resonance energy transfer (FRET)-based color change modes will be presented.

O12.2 Third-Order Nonlinear Optical Properties in Dendrimer Nanocomposites. Ying Wang, Ted Goodson and Xiao Xinglin, Department of Chemistry, University of Michigan, Ann Arbor, Michigan.


1Chemical Science and Technology Laboratory, National Institute of Standards & Technology, Gaithersburg, Maryland; 2Mechanical Engineering, University of Maryland, College Park, Maryland.

We report on the growth of nanowires and unusual hollow microtools of tungsten oxide by thermal treatment of tungsten films in a radio frequency hydrogen/argon plasma at temperatures between 550-620 °C. Nanowires with diameters of 10-30 nm and lengths between 50-500 nm were formed directly from the tungsten film. Presence of a reducing gas such as H2 was crucial in growing these nanowires as their trace quantities of oxygen necessary to form a volatile tungsten species. To verify the role of H2 as reducing agent rather than as an agent for creation of a WH species, we replaced the H2 with carbon monoxide and found that nanowires were again formed. Nanowires were also observed to grow on tungsten filaments under similar processing conditions, forming a bristle coating. A commercial tungsten coated TEM grid also converted to nanowires under the plasma treatment. Thus this approach to fabrication is quite general. Under certain operating conditions hollow microtools having edge lengths ~ 0.5 μm and lengths between 10-20 μm were observed on treated tungsten films. Preferential restructuring of the film surface into nanowires or microtools appeared to be significantly influenced by the rate of mass-transfer of gas phase species to the surface. Applications for the nanowires include field emission devices, improved STM tips, and chemical sensor films. A micromachined gas sensor containing tungsten nanowires, annealed at 500 °C, air exhibited capability of sensing trace quantities of nitric oxides (NOx).

O12.4 Ab Initio Study of Helical Silver Single-Wall Nanotubes and Nanowires. Shelly L. Eliondro and John W. Mintmire; Department of Physics, Oklahoma State University, Stillwater, Oklahoma.

In this study, we investigate the electronic structures and excitation spectra of extended silver single-wall nanotubes and nanowires exhibiting helical periodicity. The analysis is carried out within a first-principles, all-electron self-consistent local density functional approach (LDF) adapted for helical symmetry. Recent incorporation of time-dependence into our first-principles LDF method (TD-LDF) allows for the treatment of the response of a system to a time-dependent local potential, and as such, preliminary results obtained within our TD-LDF approach will also be presented. It is well known that the size and shape of silver and gold nanotubes results in the ability to tailor the optical and catalytic properties of these materials. Herein, we provide an overview of the structural classification of helical silver (or gold) single-wall nanotubes, which theoretically involves wrapping a triangular sheet of silver atoms and mapping the atoms onto the surface of a cylinder, comparable to wrapping up a grapefruit sheet for a carpaccio. Within this study, a nanowire is defined as a silver atomic chain or a silver single-wall nanotube with a silver atomic chain inserted along the axis of the tube. After discussing the geometry of these structures, we present electronic structure results obtained within the time-independent LDF approach. We then review the theoretical background and the significance of using a time-dependent approach to treat the excitation spectra. As we discuss our methodology of integrating time-dependence into our code, specific challenges that arise from treating extended systems, as opposed to molecular systems, are addressed. As a final point, we conclude with a discussion of preliminary results obtained within the TD-LDF approach. This work was supported by the US Office of Naval Research and the DoD HPCMO CHSSI program through the Naval Research Laboratory.

O12.5 Strategies for Controlling the Planar Arrangement of Micellar Templated Inorganic Nanoclusters and Their Applications in Carbon Nanotube Synthesis. Ryan Derek Bennett1, Anastassios John Hart2 and Robert E. Cohen;

2Chemical Engineering, MIT, Cambridge, Massachusetts; 3Mechanical Engineering, MIT, Cambridge, Massachusetts.

Here we report a general route that utilizes block copolymer micelles as means to create tunable inorganic nanoclusters, which then serve as catalysts for carbon nanotube growth. Our approach uses the amphiphilic block copolymer, poly(styrene-block-acrylic acid) (PS-b-PAA), which forms spherical micelles in solution that can be selectively loaded with metal ions and then spin-coated onto a substrate to create quasi-hexagonal arrays of metal-loaded PAA domains within a PS matrix. We report several strategies for varying the diameter, the center-to-center spacing, and the density of the metal-loaded block copolymer micellar domains on planar substrates.
The strategy we use to vary these inorganic nanocluster arrays include the variation of the molecular weight of PS-b-PAA, the variation of the metal loaded into the micellar solution, and the mixing of different micellar solutions. Through these routes, we demonstrate varying the diameter of the inorganic nanoclusters from 4.2 nm to 16 nm and the areal density from 10^11 to 10^14 clusters per cm². We then demonstrate the use of these inorganic nanoclusters as catalysts in a thermal chemical vapor deposition (CVD) growth of carbon nanotubes, while varying the properties of the nanoclusters and the substrates. We also demonstrate a specific example of using these nanoclusters in the process of thin-film deposition as a function of the lateral spacing of the clusters. The process continues by repeating the etching and passivation cycles. The nano-cantilevers array (100-200 nm in diameter) formed on the substrate upon the completion of the process. The possibility of utilizing this cationic or anionic surfactant can be controlled by adjusting the thickness of the sidewall oxide layer. A variety of side-wall profile can be realized by such technique, e.g. tapered or sawtooth. These nano-mechanical sensors have a representative application for measuring the mechanical force occurring in a biological system, which range from a few μN down to pN, or less.

O12.6 In situ SAXS of Zeolite Microwave Hydrothermal Synthesis. Geoff Allen Tompsett, Curt Conner, Bernard Panazzola, Sigfrid Yngvevsson, Fan Lu and Keith Jones. Chemical Engineering, University of Massachusetts, Amherst, Massachusetts; Electrical Engineering and Computer Science, University of Massachusetts, Amherst, Massachusetts; Environmental Sciences, Brookhaven National Lab, Upton, New York.

The microwave hydrothermal synthesis of silicate zeolite was monitored in-situ by small angle x-ray scattering (SAXS): a custom built waveguide reactor provided the microwave heating. This waveguide was comprised of a resonant cavity that is tuned to 2.45 GHz using both coax and waveguides to the supermicrowave. The waveguide end of the microwave was sealed with a fiber optic temperature probe for monitoring the temperature. Silicate zeolite precursor solutions of tetraethyl orthosilicate, tetraethylammonium hydroxide and water were heated temperatures between 273 and 403 K for up to 120 minutes. The SAXS patterns were simultaneously scanned during the reaction under microwaves via small holes in the side of the waveguide. The progress of the silicate zeolite formation was successfully monitored and the analysis of the SAXS patterns showed the primary particles of 2.4 nm shifted to aggregates of 10 nm in diameter, in 120 minutes at 393 K. Figure 1 shows the X-ray scattering patterns obtained a form a similar precursor solution reacted at 393 K for 120 minutes. Fig. 1 SAXS of silicate solution at 393 K with varying times.

O12.7 Creating nanostructures with controllable sidewall profile for microsensor applications. Yi Zhao and Xin Zhang. Department of Manufacturing Engineering, Boston University, Boston, Massachusetts.

Nanometer scale structures have shown their potential to be nano-mechanical sensors for sensing the otherwise indiscernible mechanical interaction thanks to their small feature size, and consequently high sensitivity. These nanostructures are usually in the form of a cantilever with a high aspect ratio, either standing upright on the substrate, or suspending laterally. Extraordinary effort has been taken for creating such structures through "top-down" or "bottom-up" techniques, while both of them have intrinsic drawbacks. For example, while in "top-down" techniques, it is difficult to assemble the structures in a desired pattern; while in "bottom-up" techniques, extra masking layers and specialized processes (e.g. deep reactive ion etching) are needed to release the structures and to control the sidewall profile. In this paper, we report a novel technique to create nanostructures with controllable sidewall profile by using reactive ion etching, with native oxide serving as the passivation layer. This technique combines the advantages of "top-down" and "bottom-up" techniques, i.e., allowing for easy patterning of the nanostructures, meanwhile minimizing the complexity of sidewall profile control. Two typical structures are demonstrated in this paper: (1) an upright nano-cantilever with a controlled sidewall profile, and (2) a laterally suspended nano-cantilever. First, the electron beam writing was conducted to pattern the nanostructures on a silicon substrate. A thin layer of chromium was deposited and being lifed off, serving as the mask for the subsequent etching. A brief reactive ion etching (CF4) was carried out afterwards with a low operating pressure, which was carefully tuned to ensure a predominantly normal incidence ion trajectory so that a vertical sidewall was achieved. After the etching cycle, the substrate was exposed to the atmosphere. The presence of fluorine on the surface produces a sharp increase in the oxide growth rate, and native oxide was formed on the sidewall and the bottom. Another cycle of etching followed. Since the anisotropy of the ion etching, the bottom oxide was removed while the side oxide remained. The process continues by repeating the etching and passivation cycles. The nano-cantilevers array (100-200 nm in diameter) formed on the substrate upon the completion of the process. The production of the laterally suspending cantilever (200nm in width), the cantilever body was formed as above. Then the operating pressure was increased to form a severe undercut below the cantilever body, to release it from the substrate. The possibility of controlling the body thickness. A variety of sidewall profile can be realized by such technique, e.g. tapered or sawtooth. These nano-mechanical sensors have a representative application for measuring the mechanical force occurring in a biological system, which range from a few μN down to pN, or less.

O12.8 Core Size Effect of Monolayer-Protected Colloids on Chemiresistor Sensors. Haick Hossan and Nathan S. Lewis. California Institute of Technology, Pasadena, California.

A promising approach to achieving low noise and controlled signal levels in chemiresistor sensors is to control the chemical inter-particle distance, and thereby obtain nearly uniform inter-particle distances in the composite film. It can in principle be achieved by use of colloidal nanoparticles that are monodisperse in size and have chemically uniform insulating capping agents. Recent efforts have shown that the resulting chemical and physical properties of the capped thiol can be controlled with the core size, and that data demonstrate that the structure and reactivity of metal-capped alkythiol change with the metal core size. Due to difficulties in direct synthesis of the monolayer-protected colloids (MPCs), such studies were limited to a narrow range of average particle diameter (e.g., < 5.2 nm for Au and < 7.3 nm for Ag). It is not clear, however, from a sensitivity and signal-to-noise viewpoints, whether one wants larger particles with fewer tunneling gaps or smaller particles which would provide more tunneling pathways. To explore such effect in core size, we developed a new approach to prepare a series of Au MPCs, having different core sizes (from 2 to 7300 nm) and similar capping monolayer, and characterized these particles in both solution phase and solid-state films. Then we probed the effect of Au MPC core size on the sensitivity, durability, reproducibility, and signal-to-noise ratio of chemiresistor sensors, under various conditions of vapor analytes. Results with a series of hexanethiol-protected Au clusters, with core sizes between 2-7300 nm, which were deposited on electrodes having a predetermined shape and inter-electrode spacing, have shown a non-monotonic correlation between the sensors response and the Au core size. Instead, in response to vapor analytes, two Gaussian-like response regions, with maximum height at 3.5 nm and 100 nm, are observed. In most cases, each size of Au MPC gives satisfying discrimination between the different analytes. The stability of these structures over more than 2000 total analyte exposures at low and high concentrations showed good reproducibility (less than 10%). The large signal-to-noise ratio in the particle size range of 2.8-5.2 nm and 50-250 nm implies that much improved detection levels are possible with this methodology. Principal components analysis, a non-linear method which captures sensor response variation in vectors orthogonal to each other and in order of decreasing variability, has been performed on these sensor response data. The principal components plot showed extremely good levels of resolution between the clusters of test analytes as observed with the 20 sensor array of hexanethiol-protected Au clusters sensors.

O12.9 Transferred to O12.7

O12.10 Molybdenum Sulphide Nanowires-Containing Catalyst: Tailoring the Selectivity by controlling the structure. Alejandro Camacho Bragado, Miguel Jose Yacaman, and Gabriel Alonso. Materials Institute, University of Texas at Austin, Austin, Texas; Chemical Engineering, University of Texas at Austin, Austin, Texas; *Ingenieria Ambiental, CIMAV, Chihuahua, Chihuahua, Mexico.

We present preliminary results on the catalytic activity of nanostructured molybdenum sulphide. The bulk catalysts were prepared by pyrolysis of molybdenum trioxide nanorods. The structural analysis of the resulting material was carried out by X-ray diffraction (XRD), scanning electron microscopy and transmission electron microscopy. Sulphides prepared by this method exibited a crystallographic structure, with a lateral size in the 3-5 nm range, and a mosaic width. The catalytic activity of the materials was tested in the gas phase reaction of isobutane, where a clear dependence on the nanowire length and catalyst morphology was observed.
poorly crystalline MoS2. XRD and electron diffraction showed the presence of two phases, molybdenum disulfide and molybdenum disulfide, indicating that sulfidation is not complete and the final product is constituted by a molybdenum disulfide core with an outermost layer of molybdenum sulfide. Elemental analysis showed and excess sulfur in the terminations of the sulfide. High-resolution electron microscopy revealed the presence of needle-like structures as well as some regular molybdenite sheets. These needles presented a very distinctive contrast in high angle annular dark field imaging that can be attributed to local electron dechanneling at these structures. There were recorded as electron energy loss spectra of the, the synthesized sulfides and commercial molybdenum disulfide. The low-loss region was identical in both cases but differences in the chemical environment of sulfur atoms were found when the sulfur edges were analyzed. The model reaction of hydrodesulfurization of dibenzothiophene was used to test the catalytic activity-selectivity of these nanowire-containing sulfides. Preliminary we could observed an enhanced selectivity towards hydrogenation when the nanowires are present.

O12.11 Electrospayed Metal Oxide films for Gas Sensing, P. K. Jha, K. K. Iyer, A. Bishop and P. I. Gouma; material science, State University of NY at Stony Brook, Stony Brook, New York.

Metal oxide films were electrospayed onto heated substrates to obtain nano-crystalline thin films in order to improve the stability and sensitivity of MoO3 and WO3. For gas sensing applications, specific crystalline phases are required with grain size stability at the operating temperature. The sol-gel sol-gel passive processing results in poor adhesion and cracking of the metal oxide films formed. Indium growth at sensing temperatures. In this process, MOX sol-gels were electrospayed using varying flow rates onto heated alumina substrates with platinum electrodes forming a porous 3D structure, providing higher surface area suitable for gas sensing applications. Structural characterization and analysis of the sensing behavior of the electrospayed MOX thin films are presented in this paper.


For metal determination in waste water, mercury-coated electrodes have been used for developing sensitivity and reliability. However they have a serious problem of Hg contamination due to their disposability. If other metals could be used for electrochemical sensor electrode, they should possess excellently sensitive and environmentally friendly characteristics. But in previous reports Hg-free electrodes couldn’t show better performance than Hg-modified electrodes. Microelectrode has a lot of advantageous characteristics (high mass transport signal to noise ratio, low ohmic drop, etc.) so when nano-electrodes were used for electrochemical sensor, serious problems, like low sensitivity of Hg-free electrode and environmental contamination of Hg electrode, could be overcome. Nano-electrode showed excellent increase of its sensitivity and didn’t have environmental problem.


Since air pollution is a serious problem, the detection of different gases in air is a matter of considerable interest and importance. With regard to the development of gas-sensitive devices, layers of metal oxides are widely employed as active compounds in gas-sensing sensors for reducing gases. In order to achieve further miniaturization of gas sensors we have focused our research on the development of metal oxides layers, in which the surface to volume ratio is drastically increased. One way to achieve high surface to volume ratio is by confinement of the metal oxides into materials with high surface area. Mesoporous materials of the M4IS family represent a viable alternative for the storage of well defined dispersions of metal oxide clusters or nanoparticles. At the same time, their regular pore structures provide an excellent accessibility for the gases to be detected. Therefore, we have introduced tin oxide species into the pores of MCM-41. These materials have been characterized by XRD, N2 sorption, and HRTEM. The host materials maintain their structure and high surface area (700-1000 m2/g) after incorporation of the oxide. DC conductivity experiments were performed under different reducing gases (CO, NOx, H2) at temperatures above 573 K to test the response of the Sn-containing mesoporous silica materials for sensor applications.


Manganese oxide octahedral molecular sieves (OMS-2) nanofibers with particle sizes as small as 6 nm were synthesized by a new soft chemistry route. The synthetic procedure is based on the four reduction of KMnO4 by H2O2 under acidic conditions. An acetic acid-containing buffer solution and HNO2 are used to control the pH of the reaction mixture. The formation process, particle size, crystallite size, crystal structure, and properties of these nanomaterials have been investigated by XRD, SEM, HRTEM, photometric titration, TGA, TPD, and N2 sorption analyses. Particle sizes of the manganese oxide nanomaterials were tailored by varying concentration of H2O2 and nature of the acid used. The crystalline phase formation, microstructure, thermal stability, and the composition of the final product were also affected by these parameters. HRTEM images reveal that the OMS-2 nanofibers are not oriented preferentially, and present significant twinning, along with discontinuity in the growth of the tunnel. Catalytic studies of these OMS-2 nanomaterials for oxidation of benzyl alcohol and fluorene have been performed. These nanomaterials show a low performance for the oxidation of benzyl alcohol and a unique catalytic activity for the oxidation of fluorene compared to OMS-2 materials prepared by conventional methods.

O12.15 Surface Characterization of Silicon Carbide Following Shallow Implantation of Palladium Ions, Claudia I. Muntele, Sergey Sarkisov, Iulia C. Muntele and Daryush Ila; Physics, Alabama A&M University, Normal, Alabama.

Silicon carbide is a promising wide-bandgap semiconductor intended for use in fabrication of high temperature, high power, fast switching microelectronic components running in hot environments with no cooling. For hydrogen sensing applications, silicon carbide is generally used in conjunction with either palladium or platinum, both of them being good catalysts for hydrogen. When such a coating is applied on the exposed surface of SiC, the chemical reaction between the catalyst and hydrogen produces a detectable change in the surface chemical potential. In the past we have produced both palladium coated SiC and palladium ion implanted SiC sensor. In this work we are investigating the effects of high-fluence, very shallow palladium ion implantation into semi-insulating silicon carbide on the sensitivity properties of the devices. We used atomic force microscopy (AFM) for monitoring the surface morphology before and after implantation, Rutherford Backscattering Spectrometry (RBS) for measuring the depth profile of the palladium distribution and the absorption of the silicon carbide crystalline lattice, and electrical measurements to determine the sensitivity to small hydrogen amounts and ruggedness of the devices when exposed to hot, oxidizing atmosphere. These tests were performed by exposing the samples to various levels of hydrogen in argon while monitoring the current flow across the p-n junction(s) and also in the surface conductivity mode with respect to time. The sensitivity of each sensor was measured at temperatures between 27 C and 800 C. The response of the SiC sensors produced by very shallow Pd implantation has revealed a completely different behavior than the SiC sensors produced before. We attribute the changes in the sensing properties to the palladium migration and forming island-like surface nanomaterials as well as quantum dots. We will present full surface morphology and electric measurements during this meeting. * Research sponsored by the Center for Irradiation of Materials, Alabama A&M University and by the Defense Nuclear Nonproliferation Research and Education Program under the contract number NAG8-1933 from NASA. ** Corresponding author: Tel.: 256-372-5895; Fax: 256-372-5868; Email: claudia@caim.aamu.edu

O12.16 The Effect of Substrate and Catalyst Properties on the Growth of Multi-Wall Carbon Nanotube Arrays. Sudheer Neelakanta, Sergey Shamonin2,1, Andrei Vyun1, Mark J. Schulz3 and Jag Sanker1; 1Mechanical and Chemical Engineering, North Carolina A&T State University, Greensboro, North Carolina; 2Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; 3Mechanical, Industrial and Nuclear Engineering, Smart Materials and Nanotechnology Laboratory, University of Cincinnati, Cincinnati, Ohio.

Self-aligned arrays of 1 mm long multi-walled carbon nanotubes (MWCNT) were grown by chemical vapor deposition (CVD) from a
gas mixture of C2H4-H2-<sub>2</sub>-H2O at 750 C. A catalytically active alumina surface coated with a thin layer of iron and supported by a Si/SiO<sub>2</sub> substrate was prepared for these experiments. In order to optimize the CNT array growth, thin Fe layers of different thicknesses were deposited on top of the alumina film using the pulsed laser deposition method. The thicknesses of the Fe and alumina films were stepped in two different forms to form a grid pattern of combinations of thicknesses. This allowed the optimal combination of the thickness of the two layers to be determined in a single experiment, for a given set of processing conditions. During the substrate preparation, the Si (100) substrate was heated at 720 C for 2 different temperatures: 200 C and 700 C. In some cases a thermal oxide under-layer below the alumina film was used. The effects of Fe thickness, alumina thickness and roughness, substrate temperature, post-annealing time, and presence of O<sub>2</sub> on the growth rate and quality of the multi wall CNNT were studied. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) were employed to characterize the morphology and the microstructure of the catalytically active metal nanolayers. Environmental scanning electron microscopy (ESEM) and AFM studies of the substrate before and after the nanotube growth revealed the critical role of the catalytic particle size, distribution, and separation by the rough alumina layer. The thickness of Fe and the roughness of the Al2O3 have a tremendous impact on the nanotube growth rate, alignment, and diameter, and need to be balanced to grow long MWNT arrays.

O12.17
Atomic Simulations of Nanoporous Anodic Aluminum Oxide. Shashi Shekar P. Adiga,<sup>1</sup> Peter Zapol,<sup>1,2</sup> and Larry A. Curtiss.<sup>1,2</sup><sup>1</sup> Materials Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Chevron Research, Argonne National Laboratory, Argonne, Illinois; <sup>3</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

Nanoporous anodic aluminum oxide (AAO) membranes, that can be prepared with atomic level control of pore dimensions and pore wall compositions, are being investigated for use in catalysis at Argonne National Laboratory. Simulation and modeling are important in understanding reactivity in confined geometry and to develop rational design strategy for these new materials. In this context, we have been using atomistic molecular dynamics (MD) simulations to study nanoporous aluminum oxide. We will present results from MD simulations of the electrochemical deposition of amorphous silicon onto the AAO. We will discuss the effect of pore radius on the surface structure of amorphous aluminum with reference to radial distribution function and coordination number of surface atoms.

O12.18
Growth of Tin Oxide Inverse Opals by Chemical Vapor Deposition. Sun Sook Lee, Kang Hyun Back, Gu Cheol Kang, Anand Gopinath and Bethanie J. H. Stadler; Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Tin oxide with periodic porosity has great potential for chemical sensors using optical spectroscopy. Tin oxide, an ionic metal semiconductor, has been investigated for transistors, electrode materials, solar cells and gas-sensing devices. For gas sensors, we have grown tin oxide into SiO2 opal structures by chemical vapor deposition from tin tetrachloride (SnCl<sub>4</sub>) and DI water. After growing, the infill was shown to be SnO2-x, coating the opal spheres as a shell to a thickness of about 30nm and giving rise to a large shift in the stop band as shown by Bragg reflectance. It was also shown that the tin oxide is homogenously deposited within the opal structure. Afterwards the glass template was removed by chemical etching, giving rise to an inverse opal. The SnO2 and inverse SnO2 have been characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), optical spectroscopy and X-ray diffraction. In addition, photonic simulations have been performed to allow optimization of the structure for highest sensitivities. The high surface areas of these structures make them particularly interesting for gas sensors.

O12.19

Ultralow-density monolithic SnO<sub>2</sub> nanotube arrays (<3-5 nm in size with <100 m<sup>2</sup>/g). The electronic structure of these arrays is studied by soft X-ray absorption near-edge structure (XANES) spectroscopy. High-resolution O K-edge and Sn M<sub>2,3</sub>- and M<sub>4,5</sub>-edge XANES spectra of monolithic nanocrystalline rutile SnO<sub>2</sub> aerogels with different surface areas (i.e., different surface-to-volume atom fractions) are compared with spectra of full-density rutile SnO<sub>2</sub>, tetragonal SnO<sub>2</sub>, and Sn. Spectra are interpreted based on the electronic densities of states in SnO<sub>2</sub> calculated with both cluster (self-consistent real-space multiple scattering) and band-structure (linear muffin-tin orbital) methods. Results show that, in contrast to the currently widely accepted picture, the photoemission data do not only affect the Fermi level position but also changes the structure of the conduction band by introducing additional Sn-related electronic states close to the conduction band minimum. These additional states are due to oxygen deficiency and are attributed to a reconstruction of SnO<sub>2</sub> nanoparticles forming the aerogel skeleton. Results of this study are important for understanding the physical processes underlying the performance of gas sensors based on SnO<sub>2</sub> nanoparticles and for predicting the behavior of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

O12.20
A New Intelligent Material Based on Long Carbon Nanotube Arrays. Yossi Shaposh<sup>1</sup>, Yun Yeo-Hung<sup>2</sup>, Mark Schulz<sup>2</sup>, Ramanand Gollapudi<sup>3</sup>, Sergey Yarmolinko<sup>3</sup>, Sudheer Neralia<sup>3</sup>, Jag Sankar<sup>3</sup>, Yi Tu<sup>4</sup> and Srivasv Subramaniam<sup>4</sup>; <sup>1</sup>Chemical and Materials Engineering, Univ. of Cincinnati, Cincinnati, Ohio; <sup>2</sup>Mechanical, Industrial and Nuclear Engineering, Univ. of Cincinnati, Cincinnati, Ohio; <sup>3</sup>Department of Chemical and Mechanical Engineering, North Carolina A&T State Univ., Greensboro, North Carolina; <sup>4</sup>none, Carpera, California.

Highly aligned multi-walled carbon nanotube (MWNT) arrays were synthesized on Si wafers. The effect of water assistance in the chemical vapor deposition process of nanotube growth was demonstrated using a thin Fe/A1203/Si02 film on a Si substrate. Quadrupole mass spectroscopy provided in-situ information of all gas partial pressures during the nanotube synthesis. Because water enhances the catalytic performance, the MWNT arrays were continuously grown for up to 3 hours. Various types of Fe patterning on the Si substrate were tested. MWNT arrays 4 mm long were grown by Chemical Vapor Deposition (CVD) from C2H2-2H2 mixtures of C2H2 at 750 deg C. Environmental scanning electron microscopy, energy dispersive spectroscopy, and atomic force microscopy were used to characterize the MWNT morphology. Transmission electron microscopy images of MWNT arrays show that the nanotubes typically have a 20 nm outer diameter and 8 nm inner diameter. Based on these results, the growth mechanism was verified and the reason for the MWNT growth stopping was investigated. To investigate applications, nanotube tubes 1 mm x 1 mm x 4 mm in size were grown and easily peeled off the Si wafer. Each nanotube contains about 1 billion individual nanotubes with 20-30 nm diameters. Electrical actuation of one MWNT tower was demonstrated in a 2M NaCl solution. MWNT tower actuators operate up to a 10 Hz frequency without significantly decreasing strain. Only 1-2 volts are applied to obtain 0.2% strain. The straight aligned nanotube tower is the reason for the higher strain. The electrical properties of buckypaper actuators. Cyclic voltammetry (CV) was performed to analyze the redox behavior of the nanotube tower used as an electrode. The CV response had a sigmoidal shape in a 6 mKHz(CN<sub>6</sub>) ferrocyanide solution. The CV response showed characteristic for biosensor development. The as-grown (no purification or functionalization) nanotube tower was cast in epoxy and the elastic modulus was evaluated using nanindentation. The Young's modulus of the epoxy material increased by a factor of two. The volume resistivity of the material was measured to be 0.11 ohm cm. The improvement in electrical actuation, elastic modulus, and electrical conductivity were much greater than the properties previously obtained by dispersing powdered nanotubes into polymers. The excellent mechanical properties, electrical sensing, and high strain generation of the nanotube array tower may become the basis for a new intelligent material.

O12.21
Structure-property relationships in chemically functionalized mesoporous carbon. Tongsoon Shin<sup>1</sup>, Glen E. Fryxell<sup>1</sup>, William D. Samuels<sup>1</sup>, Charles Johnson<sup>2</sup>, Michael H. Haley<sup>3</sup> and Gregory J. Ewing<sup>1</sup>; <sup>1</sup>Pacific Northwest National Lab, Richland, Washington; <sup>2</sup>Department of Chemistry, University of Oregon, Eugene, Oregon.

Mesoporous carbon scaffold comprise desirable support materials for catalysis, separation, and sensor applications. Particulate and internal pore surfaces are chemically modified. Work reported here is focused on the templated synthesis of these supports and their functionalization to improve adsorption capacity, specificity and surface reactivity. Hydrothermal treatment of readily available and water-soluble carbohydrate feedstocks results in formation of colloidal carbon fibers by an Aldol condensation mechanism. With step-wise expulsion of water from the carbohydrate at increased pressure, transformation to a hydrophobic phase that segregates into a
dispersion of uniform carbon spheres is observed. While a simple sugar molecule like glucose reacts over 6 hours, resident strain in the isometric, fracture zone significantly enhances the condensation reaction. In contrast, a reduced form of glucose (sorbitol) shows little tendency to decompose under similar conditions. Derivatives of glucose that contain chemically-substituted functionalities (phosphate, amine, carboxylate) react to form condensation products resulting in modifications to the attendant chemical functionality of the carbon surface. The presence of these hydrophilic groups is found to promote surface wettability thereby improving adsorption capacity. For example, metal ions can interact with surfactants via hydrogen bonding processes resulting in modifications to the attendant chemical functionality of the carbon surface. The presence of these hydrophilic groups is found to promote surface wettability thereby improving adsorption capacity.

O12.23 Structural and Spectroscopic Analysis of the Co Incorporation in to the Lattice of TiO2: Mini Rose Matheou1, Erik R. Morales2, Joel P. Enriquez1, Mari A. Cortés-Jacome2, Jose A. Toledo2. Concepcion Mejía-García1, Gerardo Contreras Puente1, Alex Punnose1 and Xavier Mathew1; 1CIE-UNAM, Temixco, Morelos, Mexico; 2Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Mexico, Mexico; 3ESFM, IPN, Mexico, Mexico; 4Physics, Boise State University, Boise, Idaho.

Development of transition metal doped TiO2 is interesting due to the possibility of formation in situ and there are recent reports of the room temperature ferromagnetism in transition metal doped TiO2. In this work we are presenting the results of our investigation on the development and characterization of the Ti1+x, Co−x O2 doped with TANNONs (transition metal nitrides) and the samples were prepared by sol-gel method and the appropriate amount of a Co salt was added during the gel formation. The formed gel was dried in vacuum and annealed at 700 °C for four hours in continuous oxygen flow. We have prepared samples with Co concentration in the range 0.5 to 2 % atomic weight. The XRD analysis showed that the samples are polycrystalline rutile TiO2 and no other phases could be observed. The grain size showed a dependence on the doping concentration; increases within which were obtained for 2% doped sample and for higher doping showed a tendency to decrease. The strain of the samples showed a strong dependence on doping concentration; increased almost linearly and it was found that the strain of a 3% Co doped sample was double than that of the undoped sample. The lattice volume also showed a dependence on doping concentration. Raman spectroscopy is a powerful tool in investigating the disorder and structural changes due to the incorporation of an ion into the host lattice. The results of the Raman analysis are correlated with the structural data obtained from XRD analysis. The Raman and IR spectra was recorded in the characteristic region of the TiO2, and additional bands are observed in doped samples indicating incorporation of Co into the lattice.


Much research emphasis recently has been on increasing the portability, selectivity, sensitivity, and adaptability of high performance liquid chromatographic (HPLC) systems, through modification of their collector columns. Multilayer carbon nanotube (MWCNTs) arrays are suggested as an ideal monolithic structure for achieving these goals due to their extremely high surface area, small pore size, and easy integration with common microfluidic techniques. This presentation shows MWCNT arrays which are being developed for use as filters and separation/concentrator columns in a (HPLC) system. Here, MWCNTs are controllably grown by patterning the catalyst layer with etched silicon channels. We have demonstrated that channels (typical cross sectional dimensions of 250 nm in width by 20 to 50 µm in length) can be easily filled by the MWCNT monolithic structure with length scales of 100µm to 10cm. The pore size and separation characteristics of these devices (based on filter length, applied pressure, and pressure drop across the array) are obtained in situ by fluorescence microscopy and spectroscopic analysis at the chip outlet.

O12.25 Spin-Spin Interactions in Cu2+ Exchanged Faujasite-X Zeolite. Chrisein B. O. Kowene, Barry Jones and David C. Doetschman; Chemistry, SUNY, Binghamton University, Binghamton, New York.

The interpretation of the EPR spectra of Cu2+ exchanged Faujasite zeolite is not straightforward. Recent literature points to the role of both the Cu2+-zeolite sites and the Cu2+-relationship to lattice Al in determining the parameters of Cu2+-spin Hamiltonian. Our work showed that at low concentration (< 8 Cu per 400 Al of zeolite), the Cu2+-EPR signals show negligible spin-spin interactions. The relative intensities of the two Cu2+-spectra observed at low Cu2+-exchange is determined by the probabilities of A1 distribution in the six-electrons of site 11. Above 8 Cu per 400 Al, both the CW EPR and the spin relaxation parameters of Cu2+-exchanged faujasite-X have contributions from spin-spin interactions.

O12.26 Addressable Assembly and Enzymatic Function of Gold-Binding Protein/Alkaline Phosphatase Molecular Constructs for Retained Activities. Torug Yacar1,2, Melvin Chin1,2, 3, Alex Den2, Canadan Tamer1,2 and Mehmet Sarikaya 1,2; 1Molecular Biology and Genetics, Istanbul Technical University, Maslak - Istanbul, Turkey; 2Materials Science and Engineering, University of Washington, Seattle, Washington; 3Chemical Engineering, University of Washington, Seattle, Washington.

We demonstrate design and engineering of a gold-binding protein genetically fused to alkaline phosphatases and present a procedure of the fabricated assembly of the construct with inherent inorganic binding and enzymatic bi-functional activity. The gold binding protein (GBP-1) is a 14- amino acid polypeptide, MHKGTQATSGTQGS that was combinatorially selected using cell surface display using mutopin, LamiB, a membrane protein, GBP-1 was further engineered and fused to alkaline Phosphatase (alkP), an enzyme responsible for phosphate removal usually from DNA and RNA. Following the expression of the genetically engineered GBP-1/alkP molecular construct in E. coli, we isolated both the recombinant and wild type proteins via osmotic shock protocol and purified through ion-exchange and gel filtration chromatography protocols. Phosphatase as well as inorganic binding activity was studied using several biochemical and imaging (atomic force microscopy) procedures. Based on the best heterofunctional activity, the 5-repeat gold binding protein (70 amino acids) was chosen for further studies. We immobilized the construct on gold nanoparticles (10-15 nm diameter) as well flat gold substrates via biotin-avidin reaction and measured the catalytic activity of the alkP spectrophotometrically by monitoring phenol formation from the reaction with pyrimidine phosphate. The enzymatic activity was absent when wild-type alkP and carbon nanoparticles without the fused GBP-1 were incubated. We fabricated micropatterned gold surfaces by using thiol-anchored polyethylene glycol that was stained using soft lithography and, thus, creating addressable hydrophilic/hydrophobic regions on the surface. Using the micropatterned substrates we directed-assembled GBP-1/alkP constructs within 5-nm diameter hydrophobic regions and demonstrated its retained enzymatic activity. The protocols developed can be of great utility for spatially distributed biosensing and bioactivity for single or more functions. This work is supported.
O12.27 Temperature Dependence of the Electronic Transition Energies in Individual Carbon Nanotubes. Stephen Cronin, Yan Yin, Andrew Walsh, Rodrigo Capaz, Alexander Stylogiorgos, Steven Louie, Anna Swan, Selim Ulun, Bennett Goldberg and Michael Tinkham; 1University of Southern California, Los Angeles, California; 2University of California, Berkeley, California; 3Boston University, Boston, Massachusetts; 4Universidade Federal do Rio de Janeiro, Caixa, Rio de Janeiro, Brazil; 5Harvard University, Cambridge, Massachusetts.

Tunable Raman spectroscopy is used to observe the optical transition energies $E_{22}$ of individual single wall carbon nanotubes over a wide range of temperatures. Varying the temperature provides a way of tuning the electronic and vibrational energies in a nanotube. By growing the nanotubes on substrates we eliminate the effects of interaction with the substrate, surfactant molecules and other nanotubes. For all nanotubes measured $E_{22}$ is observed to shift down in energy by as much as 50 meV, from -160 to 300°C, in contrast to previous measurements performed on nanotubes in alternate environments, which show upshifts and downshifts in $E_{22}$ with temperature depending on chirality. We explain the difference observed in the two measurements using two models, one based on electron-phonon coupling and another based on thermal expansion.

O12.28 In-situ Protein Detection Using a Piezoelectric Microcantilever. Joseph F. Heitman, Maria J. Borchardt, John Paul McGovern, Qing Zhu, Wan Young Shih and Wei Heng Shih; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Piezoelectric microcantilevers have been developed to perform direct detection and quantification of biological molecules in situ. Two different types of cantilevers are used in these experiments. One type of microcantilever is composed of lead zirconate titanate (PZT) layer bonded to glass, while the other is lead magnesium niobate-lead titanate (PMNPT) to copper. Both systems are characterized by specific resonant frequencies when driven by an alternating current. These resonant frequencies can be monitored and, as has been shown in previous work, the shift of the lower frequency of the resonances is related to the mass attached to the sensor tip. The monitoring of these frequencies is accomplished by monitoring the impedance of the cantilever, thus providing for an all electrical means of detection without the need for a mechanical sensor such as a silicon microcantilever. The sensitivity of the PZT-glass cantilever has been experimentally determined to be on the order of $10^{-11}$ g/Hz, while the sensitivity of the PZT-copper cantilever has been estimated to be on the order of $10^{-12}$ g/Hz. Static, as well as flow detection conditions were implemented. A prerequisite for in situ detection under the conditions of flow is that the cantilever must be insulated. It was demonstrated that a coating of MTS (methyltrichlorosilane) was sufficient to prevent the PZT-glass system from shorting in PBS (phosphate buffered saline) for a period of time in excess of two hours. Similarly, it has been shown that a coating of parylene-c can successfully insulate the PZT-copper cantilever. These cantilevers have been shown to be a sufficient tool for the detection of PSA (prostate specific antigen). Currently under investigation is the use of these cantilevers for the detection of GP120, a protein marker for HIV, and two proteins believed to be makers for breast cancer, HER-2 and the extracellular domain of αEGFR. In order to establish selectivity of these cantilevers, commercially available antibodies are used for PSA and GP120, while single chain variable fragments (scFv) provided by G. Fox (Fox Chase Cancer Center) are used for the HER-2 and αEGFR. The antibodies and scFv can be immobilized on the cantilever surface using standard bio-conjugation techniques. In addition to this, experiments are being conducted to assess whether the use of a matrix such as poly(ethylene glycol) can be used to improve the scFv to the surface through a HIS-tag(fx). This immobilization scheme will orient the scFv on the cantilever surface and increase the sensitivity of the cantilevers by maximizing the number of proteins that can be bound to the surface.

O12.29 The effect of the size of gold nanoparticles on the catalytic activity of the decomposition reaction of CH3CHO. Koji Taji, Yutaka Tai, Shiko Nagano and Jeong-Kwon Lee; AIST, Nagoya, Japan.

The composites of size-controlled gold nanoparticles (about 2-5nm in diameter) were supported on titania-coated silica aerogel were prepared. And the catalytic activity of the composites for oxidative decomposition reaction of acetaldehyde around the room temperature was measured. The composites were prepared by the following methods. Thiol-passivated gold nanoparticles prepared by the reduction of auric ion under coexistence of dodecanethiol were dispersed under carefully controlled pH environment in order to obtain thiol-passivated gold nanoparticles having objective size. The size-controlled thiol-passivated gold nanoparticles were adsorbed in titania-coated silica aerogel by immersing the aerogel powder into toluene solution of the gold nanoparticles. The aerogel was naturally dried, and then thiol capping was removed through heat treatment in air at 673K. The change of the size of the gold nanoparticles was very little in the heat treatment, so the composites of size-controlled gold nanocatalysts were prepared. Catalytic activities of the composites were measured in small fixed-bed reactor. Acetaldehyde concentrations of the effluent gas were measured by a gas chromatograph. The size of gold nanoparticles greatly affected to the catalytic activity. The results were compared with the results of low temperature CO oxidation activity, which have a maximum around 2.5-3nm, and were discussed.

O12.30 Stable and Reproducible Chain-like Assembly of Gold Nanoparticles for Surface-enhanced Raman Scattering. Takao Fukunaga1, Ryoosuke Kuramoto2, Nagisa Shinohara3, Shuzo Ikuta4, Motofumi Suzuki5 and Yasushi Mori1; 1JST Kyoto CREATE, Seika cho, Kyoto, Japan; 2Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Japan; 3Department of Micro Engineering, Kyoto University, Kyoto, Japan.

The development of nano structure produced from nanoparticles is significant. Aggregation of the gold nanoparticle in aqueous medium shows the characteristic localized plasmon resonance (LPR). Lateral aggregation of the gold nanoparticles can be used in semiconductor physics. A new system which has already been computed by Quinten and many researchers, and Creighton foresaw that such chain structure was effective as a surface-enhanced Raman scattering (SERS) substrate. However these aggregation are unstable in aqueous medium. Therefore nobody confirmed availability of the chain-like structure as SERS substrate. Using the interaction of dispersing nanoparticles, we fabricated new stable and reproducible hydrogel of gold nanoparticles assemblies which were just containing citrate capping and involved neither protecting molecule like thiol nor surfactant. The assemblies with various particle size (from 20 nm to 50 nm), particle number concentration, and propagation time of aggregation (from 1 to 30 s) were prepared. Extinction spectra of the bulk solution, activity of SERS substrate, and morphology of the aggregates were investigated. When propagation time of aggregation was 5 or 10 s under condition of NaCl 50mM, the unique LPR appeared in which the wavelength was close to that of incident laser, and large SERS intensity was observed. These wavelength of LPR of assemblies were theoretically discussed. Prepared SERS substrate was the hydrogel with the high fluidity. The end-on adsorbed ring breathing vibration peak appeared immediately, when Raman excited at 785 nm was measured by the mixing of this SERS substrate with the pyridine aqueous solution. Pyridine was determined at 50mM-2mM concentration range. The activity as SERS substrate are strengthened more than 100 times although it was fluid hydrogel. Aggregation size L and numbers of particle N in the aggregation were also counted from the TEM images. Fractal dimension $D_f = (log N / log L)$ increased from 1.2 to 1.3 depending on the growth. These facts indicate that we can observe snap shot of the propagation of chain-like growth by diffusion limited aggregation of the gold nanoparticle.
Q12.32 Controlled Growth of Gold Nanorod Arrays from Polyethylene Glycol Solution: Application to Magnetite Ferritin. Ji-Soo Kang, Mi-Min Moon and Alexander Wei; Chemistry, Purdue University, West Lafayette, Indiana.

An nanorod arrays were grown by electrodeposition in Au-baked nanoporous alumina templates modified with polyethyleneimine (PEI) as an adhesion layer. By varying the concentration of PEI and using the different molecular weight PEI, the length of nanorod arrays were highly controllable over a wide range of length. The diameter of nanorods was expected to be smaller than 100 nm with relative standard deviations below 4% for rods 300 nm to 1.7 microns. The uniform growth rate appears to be determined by the adsorbed PEI matrix, which controls the growth kinetics of the nanorods comprising the nanorods. The nanorods were retained as free-standing 2D arrays after careful removal of the AAO template, or thermally annealed within the template and released as monodisperse particles of uniform size.


Nanoporous metals formed by the electrochemical process of de-alloying possess a bi-continuous metal-vapor morphology. These materials have very high surface area to volume ratios due to the size scale of the porosity being in the nanometer regime. This characteristic makes these materials candidates for use in miniaturized sensor/sensor arrays. Simulations using the Embedded Atom Method were performed to explore the surface-stress induced strains in these nanoporous structures as well as small spherical clusters. Results of these simulations will be presented which demonstrate the importance of surface relaxation on the elastic behavior of these materials.

Q12.34 Synthesis of Nanoporous GaN Crystalline Particles by Chemical Vapor Deposition. Joao Carvalho, C. J. Wu, N. M. Gomez and J. Carlos Rojo; Department of Materials Science & Engineering, State University of New York, Stony Brook, New York.

The unique properties that porous semiconductor materials exhibit compared to their bulk counterparts have propelled the utilization of these materials in the fabrication of enhanced devices for advanced microelectronics, sensors, interfacial structures and catalysts. Among these materials, wide bandgap semiconductors (SiC, GaN, ZnO, BN, etc.), either by themselves or in combination with other materials, are expected to potentially contribute to the advancement of novel technologies in the fields of biotechnology, catalysis, and biophotonics. The actual application of these materials does, however, critically hinge on the development of processing methods able to precisely control the optical and electrical properties of the resulting porous materials. The use of nanoporous GaN particles, characterized by a high chemical and thermal stability, as an active catalytic support can potentially lead to enhanced methanol and related fuel cells as well as other heterogeneous catalytic systems. Nanoporous GaN structures can also find application as buffer layers or templates for heteroepitaxial growth of lattice-mismatched materials with low density of defects. Despite of the great potential for technologies based on nanoporous GaN, very little work has been devoted to the development of approaches to produce this material. While corrosion processes, such as electrolytic etching and anodization processes, have been commonly utilized for the fabrication of nanoporous GaN, the pore size achieved with these techniques is limited to about 300 nm. Synthesis procedures which allow for high specific surface area and well defined nanopore size are still lacking. Using a chemical vapour deposition approach based on direct reaction of Ga with NH3, nanoporous GaN particles of less than 100 nm have been synthesized. Compared to other reported approaches, this process is unique in that it results in the formation of nanoporous structures during the growth process without requiring post-growth treatments. SEM analysis of the nanoporous GaN crystalline morphology reveals a regular array of nanopores closely aligned along the [001] crystallographic directions. The morphology of these nanoporous particles seems to be strongly controlled by the growth conditions, mainly temperature flow rate, and the time of growth. The role of the substrate choice as a decisive way to control the formation of the nanostructures will also be discussed along with detailed characterization of these structures by microscopic techniques.

Q12.35 Optimisation of the Production of Magnete Nano-Particles Synthesised using the Magnetite Ferritin. Angus Bewick, Richard Jones, Oksana Kasyutich, Barnaby Warne, Eric Mayes and Mike Perry; NanoMagnetics Ltd, Bristol, United Kingdom.

The biological macromolecule Ferritin (an iron-storage protein) has long been recognized as a useful template within which to synthesise size-contrasted, functional nano-particles. The outer protein shell (dia about 12nm) confers high colloidal stability, aqueous solubility; biocompatibility; functionalisability. The material of the inner particle core (constrained by the protein shell to a maximum diameter of 8nm) can be selected to enhance the properties of the overall particle. Examples (and properties/uses) of core materials already demonstrated include: magnetite (super-paramagnetic - MRI contrast enhancement; medical diagnostics: magnetic separation); FePt, CoPt (high-anisotropy, ferromagnetic - ultra-high density magnetic recording); C60 (optical/electro-luminescence). We are particularly interested in magnetite-cored ferritin (so-called Magnetoferritin), and its applications noted above (including water purification, by forward osmosis and subsequent magnetic separation). Previous lab-scale demonstrations of magneto-ferritin synthesis have yielded some near-ideal particles amongst a spectrum of non-ideal reaction products such as: protein fragments; protein oligomers; extra-protein Fe/magnetite; particles outside the desired size distribution. Further, the stability of the aqueous particle solutions was questioned. We have attempted to optimise the synthesis of magneto-ferritin by using fractionation of the as-synthesised product to aid characterisation and to determine the yield of ideal particles. We have used and developed a two-stage fractionation process: ion-exchange column separation (to select only protein-like particles); and high gradient-field magnetic separation - HGMS (to narrow the core size distribution).

Characterisation of the as-synthesised products using NMR (gel-electrophoresis, TEM and magnetometry) shows a near-ideal magneto-ferritin particle. Long-term stability of the aqueous particle solutions has been demonstrated. The separation procedures we have used are readily scalable to produce commercially viable quantities of near-ideal magneto-ferritin.


Nano-structures, such as wires, rods, belts and tubes, whose lateral dimensions fall in the range of 1 to 100 nm, have received growing interests due to their outstanding properties and their potential applications in electronic and biological fields. The development of these new structures into functional nano-devices crucially depends on the development of new characterization techniques and theoretical models for a fundamental understanding of the relationship between the structure and properties [1]. X-ray nano-diffraction technique was employed for characterizing individual ZnO nano-belts and nano-rings. The measurements of X-ray diffraction lines from a single nano-belt were achieved by using the unique nano-diffraction technique described in [2]. The results were compared with those obtained from TEM [1] Zhao M. H., Wang Z.L., Mox S. X.; Nano Letters, 2004, 4, 587. [2] Xino, Y.; Cai, Z.; Wang, Z. L.; Lai, B.; Chu, Y. S. J. Synchr. Rad., 2005, 12(2), 124.

Q12.37 Integration of indium oxide nanowire sensors with low-power microheaters. Dainha Zhang, KYoungmin Ryu, Xiaolei Liu, Chai Li, Bo Lei and Chongwu Zhou; Electrical Engineering, University of Southern California, Los Angeles, California.

We have assembled indium oxide nanowire micro-heaters with low-power micro-heaters for detecting a broad class of chemical vapors. The sensing ability of individual indium oxide nanowires was systematically investigated at different temperatures and gas concentrations. The electrical conductance of a heated nanowire was significantly sensitive to a wide variety of chemical species including oxygen, ethanol, carbon monoxide, dimethylmethylene, and dimethylmethylene, etc. We have further demonstrated that Au-functionalized indium oxide nanowires exhibit a dramatic improvement in sensitivity toward certain chemicals due to the enhanced catalytic dissociation of the molecules on the Au nanoparticle surfaces. This transduction mechanism can form the basis for a fast, low-power sorption-based chemical sensor. Our novel approach will potentially allow for the large-scale fabrication of high-density nanosensor arrays.
O12.38
Using Surface Energies to Control Porphyrin Nanoparticle Distribution and Morphology. James Batteas1, Charles M. Drain2, Chang Xu3 and Kate Beers2; 1Department of Chemistry, Texas A&M University, College Station, Texas; 2Department of Chemistry and Center of Nanotechnology, Hunter College/CUNY, New York, New York; 3NIST, Gaithersburg, Maryland.

Surface energies have been found to be effective in controlling the surface adsorption and morphology in organic monolayers. Therefore, nanoparticles of an Fe(III) porphyrin appended with four N-polyethyleneglycolpyridinium moieties prepared in acetonitrile were deposited onto hydrophobic or hydrophobic surfaces. After solvent evaporation, the resulting aggregates were studied with atomic force microscopy. On hydrophilic Si surfaces, aggregates were found to be distributed across the surface that was in contact with the solution. The aggregate heights on hydrophilic surfaces were substantially smaller than the average size (~110 nm diameter) of the nanoparticles in solution. The observed disk-shaped materials have diameters of hundreds of nanometers, and are generally ~0.5 nm thick, corresponding to a single layer of this porphyrin on the surface. Conversely, on hydrophobic surfaces modified with self-assembled hydrocarbon monolayers, larger nanostructures are observed. Though most aggregates on hydrophobic surfaces resemble nanoparticles, i.e. have the same general dimensions as those in solution, the appearance of ~4 nm disk structures suggests the occasional rearrangement of the supramolecular organization of the aggregates. The transformation of these nanoparticles on hydrophilic surface is attributed to the strong interaction between the nanoparticles in the water/microenvironment and the surface. Mechanisms for the control of nanoparticle morphologies by varying surface energies are discussed. The interactions between various surfaces and other self-organized nanoparticles held together by weak intermolecular interactions.

O12.39
High sensitive optical detection of bio-chemicals on a silicon oxide surface based on waveguide mode. Nobuko Fukuda1, Makoto Fujimaki1, Koichi Awazu1, Kaoru Tamada2 and Kiyoshi Yase1; 1AIST, Tsukuba, Japan; 2ITT, Yokohama, Japan.

This work presents high sensitive detection of specific adsorption of proteins onto a silicon oxide surface modified by molecules with a biotin-end group. The advantages of the silicon oxide surface for a biosensing interface are inertness to bio-chemicals and ease of surface modification using silane coupling agents. The silicon oxide is also a useful dielectric material as a waveguide. The waveguide mode can be excited by irradiation of the p- or s- polarized light under total internal reflection condition. The optical configuration for surface plasmon resonance (SPR), which has been widely used for a powerful biosensing tool, is directly available for excitation of the waveguide. We fabricated the silicon oxide waveguide interface by sputtering onto a thin gold film and measured the incident angle-dependence of reflectivity using He-Ne laser. Then the s-polarized light was irradiated to the silicon oxide waveguide (760 nm) coupled with a prism, the incident angle-dependence of reflectivity showed excitation of the waveguide mode. The waveguide surface was modified by the molecules with the biotin-end group as a probe particle. Specific adsorption of streptavidin in a PBS buffer solution was monitored through time course of reflectivity change at a constant incident angle, where the waveguide mode was excited. As compared to conventional SPR system using a gold surface, high sensitive detection of the specific adsorption was achieved. In addition, we demonstrate the micro-pattern of the protein probes by micro-contact printing onto the silicon oxide surface and the waveguide mode imaging using a CCD camera.

O12.40
Evaluation of Gas Sensor of TiO2 Thin Films By CM-GFS Source. Kazuyo Oguri1, Mitsuo Iwase1, Hiroyuki Nishino1, Masahiro Yamazaki2 and Susumu Kasaki2; 1Dep. of MS, Tokai Univ, Hiratsuka, Japan; 2Tokyo National College of Technology, Tokyo, Japan.

We produced original sputter device CM-GFS source. Pt doped TiO2 thin films were deposited by CM-GFS source. The thin film that had deposited by this device was evaluated. When sputtering the Ti only, TiO2 thin films are formed in anatase structure and co-sputtering Ti and Pt, the Pt-doped TiO2 in rutile phase is formed. Particle size of the thin films was measured by SEM. The particle was grown by increasing of Pt quantity. The surface condition was evaluated by atomic force microscopy (AFM); based on the results, there is a correlation between the attractive force measured by AFM and surface free energy change estimated by contact angle of water drop. Pt/TiO2 that deposited by CM-GFS showed the photo catalyst. It was possible to apply with the gas sensor.

O12.41

We have discovered a novel property of nanomaterials - their ability to enhance protein activity and stability. We report that single-walled carbon nanotubes (SWNTs) can significantly enhance enzyme function and stability in strongly denaturing environments relative to microscale supports. Various enzymes adsorbed on SWNTs were more active and stable at high temperatures and in organic solvents as compared to conventional microscale supports such as graphite. The enhanced stability of the enzymes adsorbed onto the nanomaterial was exploited in the preparation of highly stable and active nanocomposite films that completely resist nonspecific protein adsorption. The protein-nanotube conjugates represent a new generation of highly selective, active, and stable catalytic materials. Preparing stable conjugates of proteins with nanomaterials reported here are important for a range of applications including biosensing, diagnostics, vaccines, drug discovery, and drug delivery.

SESSION O13: Catalysis and Sensor

Chairs: Wayne Daniell and Chuan-Jian Zhong

Friday Morning, December 2, 2005
Room 200 (Hynes)

8:15 AM O13.1
Impact of Structure and Morphology on Gas Adsorption of Titania-Based Nanotubes. Dong-Hoon Park1,2, Polona Usne1, Pavel Cove1, Alexandre Gloter3 and Christopher Ewels1; 1Solid State Physics Department, Institute Jozef Stefan, Ljubljana, Slovenia; 2Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia; 3Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France.

The intensive study of catalytic reactions of NOx gases on various metal oxide surfaces is largely stimulated by the problem of reducing greenhouse gas emission. The crucial material parameters in the processes of NOx removal are the active surface area and the adsorption potential. To increase active surface area a standard approach would be to prepare sub-micron metal-oxide particles. A step forward in increasing the active surface area would be to prepare particles in the form of nanotubes. Here we report on the synthesis of titania-based nanotubes and nanoribbons prepared by hydrothermal methods, as well as evaluating their structure and adsorption properties. Nanotubes were found to be hollow scrolls with a typical outer diameter of about 10 nm, inner diameter 4-5 nm and length of several hundred nm. The nanoribbons are highly crystalline, typically 40 nm in cross-section and up to a few micro-m in length. The structure of these tubes and ribbons are closely related to the family of the layered titanate (Na,H)2Ti2O5-2+n materials where the basic framework consists of TiO6 octahedra arranged in planes. Na or H ions typically layer between the titanate groups and are linked by hydroxyl groups. Samples were exposed to a NO2 atmosphere in order to test their adsorption properties using pulsed EPR. The nanotubes were found to have high active surface areas of about 250 m2/g. When exposed to NO2 gas, NOx molecules tend to adsorb to the nanotube surface via the nonbonding py orbital of the oxygen atoms. In contrast nanoribbons have much smaller active surface areas (~30 m2/g). The dominant EPR signal now comes from NO molecules adsorbed on Na+ ions. We propose that on a hydroxylated surface of nanoribbons, NO2 bind in pairs, resulting finally in NO3 and NO with some released water. NO3 in EPR silent and we thus cannot observe it in our experiments. On the other hand we clearly observe NO in all cases in nanoribbons and to a much lesser degree in nanotubes. If Na+ ions can react with this reaction, this would explain the higher concentration of NO seen in the nanoribbons where the Na concentration is higher. Nanotubes also have hydroxylated surfaces, but they have lower concentrations of Na ions available for any catalytic role. In addition the curved surface of the nanotubes may make cooperation between neighbouring NO2 molecules and surface hydroxides more difficult, lowering the probably of NO creation (except at certain special sites such as defects, sheet edges, etc). The main difference between nanotubes and nanoribbons thus seems to lie in their surface morphology, which in certain cases allows for catalytic reactions of the NO2 molecules on the titania-based surface. Our results show that titania nanotubes and nanoribbons can be strong adsorbents and even as catalysis material for NOx removal. They thus have strong and nearly immediate application potential.
Gold can be deposited as nanoparticles on a variety of metal oxides by coprecipitation, deposition precipitation, gas and liquid phase grafting of organogold complexes, and so forth. Such Au nanoparticles exhibit surprisingly high catalytic activities and selectivities for many reactions, especially CO oxidation at temperatures below 270°C and the direct gas phase epoxidation of propylene with oxygen and hydrogen. The role of nanostucture in the genesis of unique catalytic properties of Au nanoparticles is discussed for low-temperature CO oxidation. The direct role of the Au core in the support-metal oxides is indispensable for the evolution of extraordinarily high catalytic activity because the perimeter interfaces act as sites for reaction between CO adsorbed on the metallic surfaces of Au and oxygen adsorbed in the support sites but close to the perimeter. Hemispherical Au particles attached to the support at their flat planes provide larger perimeter distance. Selection of support metal oxides does not affect the catalytic activity for H2 oxidation but dramatically affects the support properties, i.e., CO oxidation. For certain practical applications that moisture promotes this reaction, the most remarkably in the cases of alumina and silica supports which are insulating metal oxides. In contrast to Pt group metal catalysts, the rate of reaction per one surface Au atom, TOF (turn over frequency), increases with a decrease in the mean diameter of Au particles. With this feature minimizing the size of metal particles is significantly rewarding for Au. It is worth noting that over Mg(OH)2 support, only small Au clusters composed of 15 atoms clusters with isosahedral structure are active. Gold nanoparticles combined with 3d transition metal oxides can detect CO and H2 by the change in the optical absorbance in the wavelength range from 300 to 700 nm. It is also possible to recognize CO from H2 by monitoring absorbance changes at two different wavelengths, for instance, at 600 nm caused by plasmon absorption over Au surfaces and at 900 nm caused by the change in plasmon density of gold nanoparticles in Au metal oxides. Supports: References 1) M. Haruta, Chem. Rec. 3, 75-87 (2003). 2) M. Date, M. Okumura, S. Tsubota and M. Haruta, Angewandte Chem. Intern. Ed. 43, 1548-1549 (2004). 3) M. Ando, T. Kobayashi, S. Iijima and M. Haruta, J. Mater. Chem. 7, 1779-1783 (1997).

9:00 AM Q13.3 Emergent Nanostructures in Conducting Polymers.
Sanjeev K. Maurice, Ning Yu, Guang Yang, and Harsha S. Kolla; Chemistry, The University of Texas at Dallas, Richardson, Texas.

A new synthetic approach is described for control of mesoscale architecture in polymers prepared by precipitation polymerization reactions. Called nanofiber seeding, and originally used for synthesizing polyaniline nanofibers, this method can now be extended to polypyrrole, PEDOT, polyphthiophene, and also to conventional (non-electronic) polymers like poly(butylcyanoacrylate). In this method, small quantities of insoluble nanofibrillar seed templates that are added prior to the onset of polymerization can dramatically change the bulk polymer morphology from granular to nanofibrillar. These nanofibers are synthesized directly in their electronically conducting doped form, e.g., the 4-probe pressed pellet conductivity values obtained arepcopolyaniline, HCl (5 S/cm), poly(3,4-ethylenedioxythiophene),Cl (30 S/cm), poly(3,4-ethylenedioxythiophene),Cl (5 S/cm) and poly(3,4-ethylenedioxythiophene),Cl (5 S/cm). Using this method, one can synthesize, rapidly and in one step bulk quantities of nanofibers of a large range of polymers from which electronic circuits and devices such as capacitors, field-effect transistors, sensors, etc., can readily be crafted. Mechanistic insight into the seeding polymerization can be gained by evaluating polyaniline as a prototype system given that fibrillar polymer growth is intrinsically favored in this system over other conducting polymers. We found that reaction conditions just prior to the onset of polymerization play an important role in the evolution of nanoscale morphology. For example, chemical oxidative polymerization of aniline in dilute aqueous acids using ammonium peroxodisulfate oxidant proceeds via the intermediary of large, colorless aggregates that act as seeds in orchestrating the bulk morphology of the polyaniline precipitate. By continuously monitoring the polymerization by static and dynamic light scattering measurements, we have observed, for the first time, the formation of 50-140 nm single aggregates during the induction period just prior to the onset of polymerization. We believe these aggregates are composed of clusters of anilinium cation and peroxodisulfate anion, and depending on the reaction conditions, they can be spherical or rod-like with the latter yielding polyaniline having bulk nanofibrillar morphology. These findings expand the role of our nanofiber seeding method, i.e., even the conventional (non-template) synthesis of polyaniline nanofibers can be viewed as a seeded polymerization system with single aggregates forming during the early stages of the reaction. The intermediary of these aggregates not only provides an important synthetic vector that could be leveraged to advantage in control of nanoscale morphology in these systems, but also adds to the growing parallels between this precipitation in polymerization reactions and inorganic biominalization processes.

9:15 AM Q13.4 Nanomaterials: Hammerheading a New Frontier.
Travis Jennings, Joerg Schlatterer, Nancy Greenbaum and Geoffrey Strouse; Florida State University, Tallahassee, Florida.

Ribozymes have become increasingly important in biochemical research because they have the potential of being powerful gene expression and viral therapy agents. Current kinetic analysis of ribozyme activity seems bound to slower but well-standardized techniques with biological techniques (PAGE, gel, radioactive labeling, etc.) We show experimentally that rapid detection of both ribozyme kinetics and insight into conformational changes in the hammerhead ribozyme is possible by monitoring energy transfer processes to small gold nanoparticles. Nanosecond energy transfer (NSET) allows for real-time monitoring of ribozyme binding, folding and cleavage events while maintaining bio-compatibility and without altering ribozymal activity. Although similar to FRET, NSET offers a number of advantages over this classical technique. A major advantage of NSET is the ability to observe simultaneous quenching events using a wide variety of organic dyes covering energies from the visible to the IR. Lifetime data of multiple dye quenching events validates the effectiveness of this technique which increases measurable distances out 2X further (>20nm) than traditional FRET and allows simultaneous analysis of ribozymal conformation on different localizations of the hammerhead moiety. This technique is effective, for but not limited to ribozyme kinetics and could include any study desiring to observe dynamic distance changes in a molecule or macromolecule.

9:30 AM Q13.5 pH Effect on the Optical Properties of Peroxo-Titanium Complexes. Ruxiong Cai1, Shun Yong Kwok2, Kiminori Itoh3 and Chang Qing Sun1; 1Singapore Institute of Manufacturing Technology, Singapore, Singapore; 2Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama, Japan; 3School of Electrical & Electronic Engineering, Nanyang Technological University, Singapore, Singapore.

The objective of this work is to study the pH effect on color change of PTC and its optical properties by using a stable PTC. This stable PTC was prepared by adding aqueous H2O2 into freshly prepared, well-crystallized titanium hydroxide cake, without adding extra acid. A fresh PTC with pH 2.21 exhibited deep green color with the pH value rising gradually during storage. It was found that the transparent orange color changes to light orange (pH 3.9), cloudy yellow (pH 5.8) and translucent pale-yellow (above pH 6.7). The pH finally levels off at a value of around 8, and the saturated PTC has been continuously stable since then. In the past, PTC was reported to be colorless in the alkaline region. Here, we clearly demonstrated that PTC shows a pale yellow color even up to pH 10.77 by adding few drops of ammonia solution (Excessive ammonia solution will cause gelation /aggregation). Lack of color in the alkaline range reported in the literature was probably due to precipitation effect during the extraction process. In order to gain more information about this stable PTC, UV-VIS spectra were measured. The freshly prepared samples had an absorption band rising at around 400 nm to higher energy, but exhibiting no maximum peak. There is a new absorption peak appears at 240 nm for the cloudy yellow samples, being similar to that of colloidal TiO2. This suggests that TiO2 particles might form during the increase in pH value. This is supported by the fact that TiO2 particles were observed under TEM for a sample with pH 8.37. The formation of TiO2 particles accelerated from pH 5.8 and above, but not in acidic conditions. In an H2SO4 acidified environment, the PTC color turned red-orange and a new absorption peak developed at 387 nm with pH 0.99. In previous work, a variety of explanations have been proposed for the color-forming species of PTC. For example, some suggested that the color was due to the presence of peroxo-disulphato titanate anion[O2Ti(SO4)2]2- in this study, we clearly demonstrated that the orange color of PTC was produced in the absence of H2SO4, suggesting that the [O2Ti(SO4)2]2- model is not reasonable. Based on the results, we can say that the UV spectrum was influenced by adding extra acid (H2SO4). The traditional quantitative measurement based on the absorption at 410 nm is likely to occur with H2SO4-PTC, but not with pure PTC. Today, the chemical composition of PTC is still unknown. We have successfully measured the influence of pH on the optical properties of PTC for the first time. More importantly, the synthesis method is simple and the PTC formed is remarkably stable. We can obtain PTC at around pH 7.8 by compared with traditional methods (< pH 1). The product can be used as an environmentally friendly precursor for thin film deposition. Further study is in progress on the coatings prepared from this material.
10:15 AM Q13.6

Synthetic control over the morphological properties of nanoparticles is critical for the development of functional architecture in nanoscience. Sensor applications will require the synthesis of heterostructures or multi-component materials that can be manipulated by external fields. Therefore, we are interested in developing 1D high aspect ratio constructs that will be tailored sensors for a variety of agents. Here, the central wire is the active element and will initially consist of Co(d) (E= S, T, T) prepared with Au or magnetic tips. This Srp will connect two electrodes. As we progress, other materials are going to be of interest and will require non-traditional precursors. Magnetic nanoparticles are being sought as the tip end for the perceived ease with which they can be manipulated by electronic fields. The forced arrangement of these nanoparticles will allow for controlled assembly of 3D structures. Magnetic materials have a variety of constituents but we are focused on the late, first row transition metal oxides, in particular, PrO4, Fe2O3, CoO, and MnO. These metal oxide nanoparticles were synthesized from their respective mesityl precursors (Fe(Mesityl)2), (Mn(Mesityl)2),, and (Co(Mesityl)2)2 (where mesityl = 2,4,6-Me3C6H2) using 1-octadecene (320 °C) and trietylphosphine as the precursors. The particles are then characterized using powder X-ray diffraction, TEM, energy dispersive spectroscopy, and SQUID as spherical (5–15 nm) and square (~20 nm) crystalline nanocores. In order to make these nanocores functional, another layer of the metal oxide surface chemistry is currently being modified to render the particles water soluble. Additional control over the morphology is being sought and the results will be discussed. In addition to our mechanical sensor, this paper also highlights the potential of these biomimetic analogues as bio-inspired arrays for apoptosis (cell death) and cancer. This work supported by the Department of Energy, Office of Basic Energy Sciences and the United States Department of Energy under contract number DE-AC04-94-AL85004 is a multidisciplinary laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

10:30 AM Q13.7

The ability to control composition and size in the synthesis of bimetallic nanoparticles is important for the exploitation of the bimetallic catalytic activity. Such nanostructured catalysts could find important applications in fuel cell reactions. This presentation discusses recent findings of an investigation of a new approach to the synthesis of gold-platinum (AuPt) bimetallic nanoparticles in aqueous solution. A range of AuPt- and PtAu- mediated catalytic AuPt nanoparticles with bimetallic compositions ranging from ~90-0% Au% and particle sizes ranging from 1 to 8 nm has been demonstrated. The composition, size, and shell properties were characterized using transmission electron microscopy, direct current plasma-atomic emission spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and electrochemical techniques. Implications of the results to the exploration of bifunctional catalysts in fuel cell reactions will also be briefly discussed.

10:45 AM Q13.8
Flame spray pyrolysis directly forms in situ thermophoretic deposition of flame-made Pt-SnO2 nanoparticles. Lutz Madler1, Albert Roeßler2, Sotiris E. Pratsinis3, Thorsten Sahn2, Alexander Gurlo2, Nicole Basran4 & Udo Weimar2. 1Department for Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland; 2Institute of Physical and Theoretical Chemistry, University of Tubingen, Tubingen, Germany.

Flame spray pyrolysis (FSP) was used to make pure and Pt-doped tin dioxide nanoparticles in one-step. The aerosol generated by the dry FSP method was directly ~ in situ thermophoretically deposited onto interdigitated Pt-electrodes to form a porous, thick film of controlled thickness within the active sensor area. Tin oxide grain size (10 nm) and a high film porosity (98 %) were preserved for all film thicknesses from 3 to 40 μm using different deposition times. The dependence of the film thickness on deposition time was theoretically estimated to enable precise control of the deposition process. Platinum doping did not affect the SnO2 grain size, crystallinity, or the porous film structure. These sensors exhibited high carbon monoxide (CO) sensor signals (8 for 50 ppm CO in dry air at 350°C), a good reproducibility, high analytical sensitivity and a remarkably low detection limit (1 ppm CO in dry air at 350°C). The in – situ platinum doping enhanced the overall sensor performance. Increasing the film thickness increased the sensor resistance and can be used to tune sensor performance.

method (DDA) have been used to model and interpret the optical properties of the released Ag nanoparticles.

11:00 AM Q13.9
Nano-sized Gas-Sensors: Synthesis and Device Application. Sajjad Mathur, Sven Barth, Hao Shen and Thomas Rueggamer, CVD Division, Leibniz Institute of New Materials, Saarbruecken, Germany.

Metal Oxide Semiconductor sensors (MOS) are gaining increasing attention due to their potential in the simultaneous and selective detection of volatile organic compounds. The density of charge carriers in MOS detectors is highly sensitive to the adsorption of chemical species, and can be modulated to induce electrical or optical signals. Metal oxide sensors are currently prepared by thick film techniques that involve application of an oxide paste between the electrodes. This method offers marginal control over film morphology and suffers from problems of poor reproducibility, porosity and weak bonding to substrates. Chemical Vapor Deposition (CVD) is a promising alternative to fabricate thin film-based sensing elements with nanoscopic features. Semiconducting materials in ultra-fine forms, in particular, one dimensional nanostructures exhibit unique transport properties due to their single crystal nature and show high potential for the gas sensing applications. We have developed a versatile route for the controlled growth of nanowires based on the decomposition of metal-organic precursors in liquefied metal catalysts. Easy regulation of precursor feedstock and pre-defined chemical composition of the source material allows tuning the microstructure of the CVD deposits. Tin oxide nanostructures of different morphologies such as, grains, platelets and nanowires were synthesized by CVD of tin tetra-ethyl-butoxide on alumina substrates with SnO2 films. The structural features were controlled by adjusting the precursor feedstock, deposition temperature, and the size of catalyst nuclei acting as template in nanowire growth. We have investigated the sensitivity of different SnO2 nanostructures towards reducing gases. Comparative evaluation of gas-sensing properties revealed that nanowires possess high sensitivity and fast response, when compared to granular nanostructures. The differential gas-sensing behaviour was related to the Hall mobility, wettability and surface area of the examined surfaces. Enhanced response of nanowires can be attributed to the reduction of grain boundaries and the nature of the depletion layer formed after the adsorption of gas molecules. Furthermore, the influence of wire diameter and dopants on the sensitivity of 1D nanostructures was investigated. Gas sensors based on tin oxide were fabricated by growing different nanostructures directly on sensor platforms. In addition, tin oxide nanostructures of different diameters were used to construct miniaturized optical switches, which could be address by using UV light. A brief account of our activities on the processing of metal oxide nanowires and their application as gas sensors and photo-detectors will be presented.