

# 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.**

Ludovico M. Dell'Acqua-Bellavitis, Jake D. Ballard, Robert Vajtai, Pulickel M. Ajayan and Richard W. Siegel; Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York.

Ex-situ transmission electron microscopy (TEM) was performed on catalytically-grown multi-wall carbon nanotubes. Two types of catalyst-nanotube wall interfaces were identified - respectively 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 - twist 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 pyrolyze 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 and the Nanoscale Science 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 stabilization, destabilization, and open-end 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 aligned carbon nanotubes. A study based on in situ diffractography, *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<sup>1,2</sup>, Xiao Zhong Ji<sup>1</sup>, Anthony Contreras<sup>1,2</sup> and Robert Rioux<sup>1,2</sup>; <sup>1</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>2</sup>Lawrence 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 we either assembled on a flat oxide substrate or encapsulated 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. After removal of the polymer, reaction studies are 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 (H<sub>2</sub>/O<sub>2</sub>, CO/O<sub>2</sub>) are carried out over a platinum thin film (5-8 nm) deposited on a semiconductor (TiO<sub>2</sub> 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 3 electrons for 4 product molecules could be detected. Hot electrons that were detected form on an ~20 femtosecond time scale during exothermic processes at metal surfaces, which is responsible for the lack of molecular excitations at the same surface that have much slower dynamics. The electron 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

Gurevich<sup>1</sup>, V. M. Kozhevnikov<sup>1</sup>, I. N. Yassievich<sup>1</sup>, D. A. Yavsin<sup>1</sup>, T. N. Rostovshchikova<sup>2</sup> and V. V. Smirnov<sup>2</sup>; <sup>1</sup>Ioffe Institute, St. Petersburg, Russian Federation; <sup>2</sup>Chemistry Department, 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 metal nanoparticles (the 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 10<sup>5</sup> product mole/metal mole . h) catalytic activity measured in several chlorohydrocarbon conversions (Cu, Ni) and hydrogenation (Ni, Pd) reactions. In all the reactions, strong dependencies 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 inter-particle or particle-support tunnel electron transitions) 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 phenomenon of particle interaction (related with their charging) opens up a new way for managing the catalytic properties of immobilized metal nanoparticles.

**9:15 AM O1.4**

**Catalytic Thin Films by Co-deposition of Gold and Anatase.**

Nancy J. Dudney, Albina Y. Borisevich, Andrew R. Lupini and Gabriel M. Veith; Condensed Matter Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

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 crystallinity 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 O<sub>2</sub>/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 reactor to monitor the reaction under conditions of different 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 reveal gold incorporation as both isolated atoms and as nano-clusters in the anatase. For denser 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.** Puxian Gao and Zhong Lin Wang; School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Structurally, semiconducting and piezoelectric zinc oxide has two important structure characteristics: the multiple and switchable growth directions: <01-10>, <2-1-10> and <0001>; and the {0001} polar surfaces. Syntheses of novel 1D ZnO nanostructures and the fundamental physical and chemical understanding of the growth process 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 nanobelts [1-3], nanorings [1], nanocantilevers [2], nanosprings [3], nanopropellers [4] and nanoarchitectures [5] such as various types of nanorings, nanobows, platelet circular structures, etc.. The growth mechanism is proposed to be the self-balance between high elastic energy 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, pressure and duration time, especially the pre-growth pressure level, polar surface dominated single crystal ZnO nanosprings have been successfully synthesized at high yield (> 50%) [7]. Our experiments indicate that doping is not necessary for forming the polar surface dominated nanosprings and nanoloops, but a pre-growth low pressure seems to be the key. The nanobelts that form the nanosprings grow along [2-1-10], and the ones that form the nanoloops/nanospirals grow along [10-10]. It is suggested that planar defects are usually present in the polar surface dominated nanobelts. This work makes it possible to synthesize high purity, high yield nanosprings, opening the door for systematically understanding the properties and exploring the applications of semiconducting and piezoelectric nanosprings of ZnO. 1) "Single-crystal nanorings formed by epitaxial self-coiling of polar-nanobelts", X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang, Science, 303 (2004) 1348. 2) "Induced growth of asymmetric nanocantilever arrays on polar surfaces", Z.L. Wang, X.Y. Kong and J.M. Zuo, Phys. Rev. Letts. 91 (2003) 185502. 3) "Spontaneous polarization-induced nanohelices, nanosprings, and nanorings 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) "Nanoarchitectures of semiconducting and piezoelectric zinc oxide", P. X. Gao and Z. L. Wang, J. Appl. Phys., 97 (2005) 044304. 6) "Substrate atomic-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 nanospring of ZnO", P. X. Gao and Z. L. Wang, Small, 2005, in press. 8) Research sponsored by NASA, NSF and DARPA. 9) Details can be found at: [www.nanoscience.gatech.edu/zlwang](http://www.nanoscience.gatech.edu/zlwang). \*email: [zhong.wang@mse.gatech.edu](mailto:zhong.wang@mse.gatech.edu)

#### 10:15 AM O1.6

**FTIR Characterization of CO Adsorption on Silica-Supported AuPt Nanoparticles.** Derrick Mott, Andrew Smith, Jin Luo and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

The understanding of the surface properties of gold-based alloy nanoparticles is essential for exploiting their unique catalytic properties. This presentation reports findings of 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 assembled on silica supporting materials, and calcinated 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 distinctively 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 \*O1.7

**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 feedstocks for fuel cells, and (b) the direct oxidation of hydrogen with oxygen to form hydrogen peroxide. The preparation and characterisation of active catalysts for these applications will be described. The preparation method is found to be critical for the preparation of stable catalysts. In both cases the way in which the catalysts are calcined is found to be the major factor controlling their catalytic performance.

#### 11:00 AM O1.8

**Steam Reforming of Propane over Nanostructured Complex Oxide Catalysts.** Hong He and Jackie Y. Ying; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Two new classes of catalysts, barium hexaaluminate (BHA) supported catalysts and nickel aluminates, 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-mediated sol-gel processing, and coated or doped with nickel. Nanocrystalline nickel aluminates with different

Ni/Al ratios were prepared by chemical co-precipitation. For the steam reforming of propane, excellent catalytic activity and hydrogen selectivity were achieved by the reverse microemulsion-derived 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 impregnated and vapor-grafted with noble 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 O1.9

**Active site Identification for Vinyl acetate Synthesis on Pd-based Catalysts.** Dheeraj Kumar, Mingshu Chen, Cheol Woo Yi, Yifan Han, Kai Luo and David Wayne Goodman; Chemistry, Texas A&M University, College Station, Texas.

Vinyl acetate (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 regarding 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/SiO<sub>2</sub>(d<sub>Pd</sub>:4nm) < 1 wt% Pd/SiO<sub>2</sub>(d<sub>Pd</sub>: 2.5nm). Moreover, the addition of Au to Pd/SiO<sub>2</sub> catalysts significantly enhances the VA formation rate and selectivity. Infrared reflection absorption spectroscopy (IRAS) of CO on Pd/Au(100) and Pd/Au(111) substantiates the presence of Pd as isolated monomers on a Au-rich surface. A pair of Pd monomers is the most favorable active site for the formation of VA. The spacing between the two active Pd monomer pairs is critical, as evidenced by the relative rates of VA formation on Pd/Au model catalysts, i.e. Pd/Au(111) < Pd/Au(100).

#### 11:30 AM O1.10

**Titanate Nanotubes as Precursor for TiO<sub>2</sub> Nanorods and as Catalyst Support for Active Metal Oxides.** Jun-Nan Nian<sup>1</sup>, Shin-An Chen<sup>1</sup> and Hsisheng Teng<sup>1,2</sup>; <sup>1</sup>Chemical Engineering, National Cheng Kung University, Tainan, Taiwan; <sup>2</sup>The Center for Micro/Nano Technology Research, National Cheng Kung University, Tainan, Taiwan.

Nanotubes prepared by treatment of TiO<sub>2</sub> in NaOH with subsequent acid washing can serve as precursor for TiO<sub>2</sub> nanorods and as catalyst support for active metal oxides. The present work has found that hydrothermal treatment of titanate nanotube suspensions under an acidic environment resulted in the formation of single-crystalline anatase nanoparticles with a specific crystal-growth direction. The crystal size of the anatase nanoparticles obtained from the hydrothermal treatment increased with the pH of the suspensions, and nanorods with an aspect ratio up to 6 and a long axis along the anatase [001] were obtained at a pH slightly less than 7. A mechanism for the tube-to-rod transformation has been proposed on the basis of the crystalline structures of the tubes and rods. The local shrinkage of the tube walls to form anatase 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 in catalysis, a process was developed to prepare high activity catalysts by loading active metal ions on large surface area TiO<sub>2</sub>. Cu-intercalated nanotubes can be obtained by adding Cu(NO<sub>3</sub>)<sub>2</sub> during the hydrothermal NaOH treatment on TiO<sub>2</sub>. Upon calcination the nanotubes transformed to large surface area TiO<sub>2</sub> aggregates containing highly dispersed Cu. The Cu-planted TiO<sub>2</sub> was shown to have high activity in selective catalytic reduction of NO with NH<sub>3</sub>.

#### 11:45 AM O1.11

**Nanoholes Formed in Silicon by Wet Etching using Metal Particles as Catalyst.** Kazuya Tsujino and Michio Matsumura; 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 H<sub>2</sub>O<sub>2</sub> 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 30 nm to 100 nm, which were 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 H<sub>2</sub>O<sub>2</sub> concentration on the etching is also demonstrated. 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<sup>-4</sup>M AgClO<sub>4</sub> and 10<sup>-3</sup>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 H<sub>2</sub>O<sub>2</sub> for 1 min. On the top of the surface, a microporous layer of about 100 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 sank into silicon and formed the cylindrical holes. 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 H<sub>2</sub>O<sub>2</sub> 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 positive charge carriers which are generated in silicon when excess H<sub>2</sub>O<sub>2</sub> is present in solution, and that the nanoholes are produced by other chemical species, such as OH radicals.

#### SESSION O2: Biosensors I

Chairs: F. P. Zamborini and Chuan-Jian Zhong  
Monday Afternoon, November 28, 2005  
Room 200 (Hynes)

#### 1:30 PM O2.1

**Deposition of Rare-Earth Doped Nanophosphors on Multi-Wall Carbon Nanotubes for Biomedical Diagnosis and Treatment.** Wei Wang<sup>1</sup>, Jie Lian<sup>2</sup>, Guokui Liu<sup>3</sup>, Peng He<sup>1</sup>, Lumin Wang<sup>2</sup>, Rodney C. Ewing<sup>2</sup> and Donglu Shi<sup>1</sup>; <sup>1</sup>Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; <sup>2</sup>Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

Surface multi-functionalization of nanoparticles or nanotubes 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 diagnosis. Here, we present a novel solution method for the deposition of nano-sized europium doped Y<sub>2</sub>O<sub>3</sub> on the surfaces of multi wall carbon nanotube (MWCNTs). The surface morphologies and microstructure have been characterized by high resolution transmission electron microscopy (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 new higher-order architectures. These 'bricks and mortar' assemblies feature structural and dynamic attributes that can be tuned to provide new materials and chemical properties. The application of this self-assembly strategy to the creation nanocomposites and bionanocomposites 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 Aubin<sup>1</sup> and Kimberly Hamad-Schifferli<sup>2,1</sup>; <sup>1</sup>Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>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 gold nanoparticle 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 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 also probe non-specific adsorption between the nanoparticle and protein.

#### 3:30 PM O2.4

**Chemical and Bio-Sensing Properties of Silicon Nanowires.** Shuit-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 matrixes 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, H-terminated SiNWs are shown to be unusually reactive that 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 glucose oxidase 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, AuCl<sub>3</sub>, and thioacetic acid, respectively. The sensor shows a wide linear detection range up to 1 microMole BSA, high sensitivity (79 mA/mmol), and good selectivity. Further, long SiNW yarns were similarly modified with AuCl<sub>3</sub> to serve as sensor to detect calf thymus DNA via CV, which shows good sensitivity and a wide linear range up to 500 microgram/mL.

#### 3:45 PM \*O2.5

**Biphasic Polymer Nanocolloids.** Kyungho Roh<sup>3</sup>, Sonsoles Olano<sup>1</sup>, David C. Martin<sup>2,3</sup> and Joerg Lahann<sup>1,2,3</sup>; <sup>1</sup>Chemical Engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>Macromolecular 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 in micro/nano-objects introduces an additional design parameter - 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, their 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 electrohydrodynamic jetting of parallel polymer solutions under the influence of an electrical field. Electrified jetting is a process to generate liquid jets by use of 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 nano-objects 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 materials distribution at the nanoscale. Moreover, the individual phases 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 nanocolloid may enable the design of multicomponent carriers with interesting properties for drug delivery, molecular imaging, or guided self-assembly.

#### 4:15 PM O2.6

##### Surface-enhanced Raman Scattering from Self-assemblies of Core/shell Bimetallic Nanoparticles. Linyou Cao<sup>2,1</sup>, Tao Zhu<sup>1</sup>

and Zhongfan Liu<sup>1</sup>; <sup>1</sup>College of Chemistry and Molecular Engineering, Peking University, Beijing, China; <sup>2</sup>Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

To prepare morphology-controlled substrates is central for exploring the origin of Surface-enhanced Raman scattering (SERS) and for applying SERS as powerful analytical tool. Herein we report the fabrication of uniform self-assemblies Au(core)/Cu(shell) nanoparticles with controlled structures via electrochemical copper deposition onto preformed self-assembled gold nanoparticles monolayer. And we demonstrate using the self-assemblies of core/shell bimetallic nanoparticles as substrates for Surface-enhanced Raman Scattering of p-aminothiophenol (PATP) molecules. Chemical and electromagnetic effect involved in the Raman enhancement can be separated from each other and both get separate analysis. The experimental result besides indicates the control of optical properties via such core/shell bimetallic nanostructures.

#### 4:30 PM O2.7

##### The Aspect Ratio Dependence of the Fluorescence of Gold Nanorods: An Experimental and Theoretical Study.

Susie Eustis and Mostafa 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 the emission from gold nanorods of various aspect ratios in the range between 2.6 (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 non-enhanced 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 Reagentless 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 bioconjugates, a modular method for small-molecule detection by semiconducting nanoparticle bioconjugates has been difficult. Here a method 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 maltose binds to maltose binding protein 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 +440 mV *versus* NHE that, proposedly, 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 interactions and a reporter of maltose binding. Four different surface-cysteine, Ru(II)-attached maltose binding proteins have been used for maltose dependent CdSe emission intensity studies. With 3.0-3.5 nm diameter CdSe nanoparticles, all four ruthenated maltose binding proteins display similar increases in CdSe emission intensity (~140%) upon saturated maltose binding

and maltose affinities ( $K_a \sim 1.6 \times 10^7$  M<sup>-1</sup>). The only difference between these four systems was the sample-to-sample variation in maltose-dependent responses. 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 extension of this system using CdSe/ZnS core-shell nanoparticles will be discussed.

SESSION O3: Poster Session: Nanoparticles and Nanostructures in Sensors and Catalysis I

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<sup>1</sup> and Arup Kumar Raychaudhuri<sup>1,2</sup>; <sup>1</sup>Physics, Indian Institute of Science, Bangalore, Karnataka, India; <sup>2</sup>Physics, 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 mostly depend on the MnO<sub>6</sub> octahedra. Any change of the Mn-O-Mn bond angle or length can change its property. Hydrostatic strain and biaxial strain greatly affects its ferromagnetic transition temperature, T<sub>C</sub>. 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 Jahn-Teller distortion around the Mn<sup>3+</sup> ions, which can be tuned by biaxial or uniaxial stress. We have done our study on La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> and La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub> polycrystalline films grown on Silicon. Chemical solution deposition technique was followed for the preparation of the films. Controlled straining of the film on the Si substrate was produced 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 ( $\Delta R/R$ ) 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. Liudmila A. Pozhar, 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 semiconductor quantum dots, atomic clusters, artificial atoms and molecules, etc.) in external electro-magnetic fields. Explicit linear (with respect to the fields) contributions to the longitudinal and transversal quantum conductivities (LLC and LTC, respectively), generalized susceptibility, and dielectric and magnetic susceptibility tensors have been derived in terms of the equilibrium retarded two-time temperature Bogoliubov-Tyablikov's Green functions (BTGFs). The Fourier-images of these functions satisfy an (infinite) system of algebraic equations (due to Zubarev and Tserkovnikov, 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

been discussed in the context of experimental data available for larger GaAs- and InAs-based semiconductor quantum dots. [1]. L.A. Pozhar, Charge Transport in Inhomogeneous Quantum Systems in Weak Electro-Magnetic Fields: Two-Time Green Function Approach (2005, in press; see also cond-mat/0502476, <http://www.arXiv.org>).

### **Q3.3**

**Enhanced Hydrogen Sensing at Room Temperature by Pd-Functionalized ZnO Nanorods.** Li-Chia Tien<sup>1</sup>, Hung-Ta Wang<sup>2</sup>, Patrick Sadik<sup>1</sup>, Byoung Sam Kang<sup>2</sup>, David Norton<sup>1</sup>, Fan Ren<sup>2</sup> and Stephen Pearton<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, University of Florida, Gainesville, Florida; <sup>2</sup>Chemical 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 change in conductance after exposure of hydrogen concentrations in N<sub>2</sub> of 10-500 ppm by five larger than nanorods without Pd. The detection of hydrogen down to <10 ppm, with relative response of > 2.6% at 10 ppm and > 4.2% at 500 ppm H<sub>2</sub> in N<sub>2</sub> 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.

### **Q3.4**

**Controlled Synthesis of Ag<sub>2</sub>Se and Cu<sub>2-x</sub>Se Nanoparticles from Single Precursor [(Ph<sub>3</sub>P)<sub>3</sub>M<sub>2</sub>(SeC{O}Ph)<sub>2</sub>] (M = Ag, Cu).** Meng Tack Ng and Jagadeesha J. Vittal; Chemistry, National University of Singapore, Singapore, Singapore.

Orthorhombic Ag<sub>2</sub>Se (nanocubes and faceted nanocrystals) and cubic Cu<sub>2-x</sub>Se (twinned nanocrystals, nanorods and faceted nanocrystals) nanoparticles have been synthesized by thermolysis of the corresponding phosphine terminated selenocarboxylates, [(Ph<sub>3</sub>P)<sub>3</sub>M<sub>2</sub>(SeC{O}Ph)<sub>2</sub>] (M = Ag, Cu) in suitable surfactants. The morphology and the size of the synthesized Ag<sub>2</sub>Se nanoparticles are found to be strongly dependent on the heating duration, temperature and the amount of HDA (hexadecylamine) added. A systematic study of the shapes of the Ag<sub>2</sub>Se nanoparticles indicates that the concentration of nuclei in the reaction solution is responsible for the final morphology of the Ag<sub>2</sub>Se nanoparticles. Meanwhile, the morphology of the Cu<sub>2-x</sub>Se nanoparticles is mainly depends on the nature of the surfactants. These nanoparticles are characterized by X-ray powder diffraction (XRPD) and high resolution transmission electron microscopy (HRTEM).

### **Q3.5**

**One-Step Flame Synthesis of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> Storage Reduction Catalysts.** Reto Strobel<sup>1,2</sup>, Marco Piacentini<sup>2</sup>, Marek Maciejewski<sup>2</sup>, Lutz Madler<sup>1</sup>, Alfons Baiker<sup>2</sup> and Sotiris E. Pratsinis<sup>1</sup>; <sup>1</sup>Particle Technology Laboratory, ETH Zurich, Zurich, Switzerland; <sup>2</sup>Institute for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland.

Engines operating under lean conditions exhibit higher fuel efficiencies than nowadays stoichiometric engines. However, in the presence of excess oxygen in the exhaust gas, conventional three-way catalysts are not capable to remove NO<sub>x</sub> sufficiently. In the NO<sub>x</sub> storage-reduction (NSR) concept NO<sub>x</sub> is stored under lean conditions and reduced into N<sub>2</sub> during fuel rich periods. Pt/Ba/Al<sub>2</sub>O<sub>3</sub> 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 NO<sub>x</sub> was investigated by a NO-pulse technique. Depending on the nozzles geometry, the use of two separate nozzles, one as aluminium and the other as barium source, resulted in the formation of individual Al<sub>2</sub>O<sub>3</sub> and crystalline BaCO<sub>3</sub> 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 //bulk-like// behaviour (decomposition above 900 °C) behaviour was observed.

### **Q3.6**

**Ability of Cathodoluminescence Measurement for Testing SnO<sub>2</sub> Films and Powders Synthesized for Gas Sensor Applications.** Ghenadii Korotcenkov<sup>1</sup>, Mihail Nazarov<sup>1</sup>, Vladimir Brinzari<sup>1</sup>, Albert Cirera<sup>2</sup>, Albert Cornet<sup>2</sup>, Kengo Shimano<sup>3</sup> and Noboru Yamazoe<sup>3</sup>; <sup>1</sup>Lab. of Micro- and Optoelectronics, Technical University of Moldova, Chisinau, Moldova; <sup>2</sup>Dept. of Electronics, University of Barcelona, Barcelona, Spain; <sup>3</sup>Faculty of Engineering

Sciences, Kyushu University, Fukuoka, Japan.

Thin (30-100 nm) nano-sized SnO<sub>2</sub> films doped by one of the metals from following rank - Fe, Co, Ni, Cu (0-16 wt %) were deposited by spray pyrolysis. SnO<sub>2</sub> 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. 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 grown 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 %) drastically changes the shape and intensity of cathodoluminescence spectra as compared with undoped SnO<sub>2</sub>. Considerable concentration of additives, apart from additives of Co, reduces the CL intensity in all spectral range of measurement. As a rule nanostructured SnO<sub>2</sub> with grain size <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.

### **Q3.7**

**Fabrication of Photonic Crystal Biosensors using Surface Structure Imprinting of Nanoporous Glass.** Ian Block, Leo L. Chan and Brian T. Cunningham; Electrical & Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

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 4x 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 nanoglass-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.

### **Q3.8**

**Effect of Zinc Oxide Nanocrystals in Mediums Containing E.coli and C. Xerosis Bacteria.** Javier Avalos<sup>1</sup>, Triana Merced<sup>1</sup>, Omayra Rivera<sup>1</sup>, Stephanie Santos<sup>1</sup>, Nicole Villalba<sup>1</sup>, Yahira Baez<sup>1</sup>, Jose Gaudier<sup>1</sup>, Oscar Perales-Perez<sup>2</sup>, M. S. Tomar<sup>2</sup>, A. Parra-Palomino<sup>2</sup> and Amarilis Ruiz-Mendoza<sup>2</sup>; <sup>1</sup>Science and Technology, Metropolitan University, San Juan, Puerto Rico; <sup>2</sup>General 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 nanosize 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 synthesized 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 suspension of nanoparticles of Zinc Oxide, shows 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 nanoparticles (standard curve). A change in the period life of the bacteria (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 particles is shown all along over 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.

### **O3.9**

**Formation of Water at a Pt(111) Surface: A Study using Reactive Force Fields (ReaxFF).** Markus J. Buehler, Adri van Duin, Boris Merinov and William Goddard; Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

From numerous experimental studies, it is well-known that Pt plays an important role as catalyst in the process of water formation based on molecular oxygen and hydrogen. However, to our knowledge, no direct atomistic simulation has been performed to show the effect of catalysts at finite temperature. To fill this gap, we have carried out finite temperature atomistic studies of water formation at Pt surfaces using a new first principles based reactive force field (ReaxFF) capable of describing the complex chemistry of water formation at Pt surfaces. We demonstrate that ReaxFF is a useful concept to bridge the gap between purely quantum mechanical approaches (e.g. DFT) to more macroscopic descriptions of atomic interactions (e.g. non-reactive force fields such as TIP or SSD). In contrast to purely quantum mechanical methods suitable for dynamical calculations (e.g. CPMD), ReaxFF can be used to model the dynamical trajectory of thousands of atoms over a time span of several nanoseconds. To elucidate the mechanism of water formation at a Pt(111) surface, we perform a series of ReaxFF molecular dynamics (MD) simulations at different temperatures. In agreement with experimental observations, we find that water formation without the Pt catalyst leads to highly explosive reactions. In contrast, presence of the Pt catalyst yields better controlled reaction conditions and much higher reaction rates. Results of our calculations clearly demonstrate the catalytic effect to enhance chemical reactions. Further, by performing a series of calculations with distinct starting configurations, we obtain statistically meaningful trajectories that allow us extracting the rate constants of water formation as a function of temperature. These numerical results enable us to estimate the activation energy of water formation. We find reasonable agreement of the resulting activation barrier compared with quantum mechanical and experimental data. We also address the effect of surface defects such as steps on the water formation rate. Similar computational approaches as the one described in this paper could be applied to other systems and may help to understand fundamental processes at reactive gas-solid interfaces.

### **O3.10**

**Template-Directed Synthesis of Titania Nanowires and Nano-Tubes Using Aqueous Precursors at Near-Ambient Temperature.** Jing-Jong Shyue, Rebecca E. Cochran and Nitin P. Padture; Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

Titania nanowires and nano-tubes can be used as nanoscale building blocks in a variety of advanced applications such as photocatalysis and devices such as solar cells. In the present work we have synthesized titania nanowires and nano-tubes inside anodized aluminum oxide (AAO) nano-hole templates using aqueous precursors at near-ambient temperature. We have used dilute hexafluorotitanate precursor (pH 2.5, temperature 45 degree-C), for the first time, to produce titania nanowires inside AAO templates by simple dipping. By modifying the wall-surfaces of the AAO template with octadecyltrichlorosilane (OTS), we were able to retard the titania-deposition kinetics, which results in the formation of titania nano-tubes. This makes the hexafluorotitanate solution a very versatile precursor in this context.

Detailed mechanisms of titania nanowires and nano-tubes deposition will be presented and discussed. The AAO template is dissolved in strong base to release the titania nanowires and the nano-tubes. The overall diameter and length of the nanowires and nano-tubes are found to be  $\sim 200$  nm and  $\sim 20$   $\mu\text{m}$ , respectively, with nano-tubes wall thickness of  $\sim 10$  nm. The titania is found to be nanocrystalline nature, with grain size ranging from 2 to 5 nm. The titania nanowires and nano-tubes, in conjunction with focused ion beam (FIB), have been used to fabricate devices for electrical properties measurements. Current-voltage and chemical-sensing properties of individual titania nanowires and nano-tubes will be presented, together with a discussion of structure-properties relations.

### **O3.11**

**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 nanoparticles with almost same size as starting particles were obtained. However, that process had some problems as time consuming and inhomogeneous adsorption. So we tried to apply more convenient method. The support materials were soaked into toluene solution of thiol-passivated gold nanoparticles, naturally dried and then thiol capping was removed by heat treatment in air at 673K. 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 had equal or superior 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. Titania-coated silica aerogels and xerogels 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 situation 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 xerogel 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 change of 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.

### **O3.12**

**Self Assembled Silver Nanoparticles on Nanostructured Surfaces for Molecular Detection by Surface Enhanced Raman Scattering.** Surojit Chattopadhyay<sup>1</sup>, Hung Chun Lo<sup>1,2</sup>, Kuei Hsien Chen<sup>1,3</sup>, Shih Chen Shi<sup>2</sup> and Li Chyong Chen<sup>3</sup>; <sup>1</sup>Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; <sup>2</sup>Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; <sup>3</sup>Center 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 (SiNNT), aluminum nitride nanotips (AlNNT), nanorods (AlNRR) 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 nanoparticles on the one dimensional nanostructured surfaces are SERS active. Molecules 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 nanostructured substrates and the extreme high density of the nanoparticles 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  $10^5$  to  $10^8$ .

### **O3.13**

#### **Controlling the Shape and Length of Gold Nanorods and Monitoring the Growth of Rod Using XAS. Haoming Chen,**

<sup>1</sup>Department of Chemistry, National Taiwan University, Taipei, Taiwan; <sup>2</sup>Catalysis Research Center, Hokkaido University, Sapporo, Japan; <sup>3</sup>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 one-dimension rod was observed, 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  $\mu\text{m}$ , 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 then gold atoms were deposited on the surface of gold seeds 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 Catalysed by Pd Ion Implantation into Si(100). Praveen K. Sekhar<sup>2</sup>, Dinesh K. Sood<sup>1</sup> and Shekhar Bhansali<sup>2</sup>; <sup>1</sup>School of Electrical & Computer Engineering, RMIT University, Melbourne, Victoria, Australia; <sup>2</sup>Department 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 drop of a catalyst metal. In this work, we have used ion implantation of Pd ions into silicon (100), through a mask, to form nanoclusters of Pd to act as such catalysing seeds. Pd ion implantation was performed with a MEVVA (metal vapour vacuum arc) ion implanter. The lowest possible extraction voltage (of 10 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 substrate held at room temperature to produce identical and well separated zones of ion implanted regions. Dose was varied from  $5E12$  to  $3E16$  Pd ions/cm<sup>2</sup>. 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  $\text{^\circ C}$  were chosen on the basis of Pd-Si phase diagram. After growth, the samples were analysed using scanning electron microscopy, Energy Dispersive Spectrometry (EDS), X-ray diffraction, Rutherford backscattering spectrometry and TEM. After heating at 1100  $\text{^\circ C}$  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  $\mu\text{m}$  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 has been shown to be valid for this 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 Si vapour being swept across by the carrier 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 SnO<sub>2</sub> Small Grains. Anna Maria Mazzone, IMM, Sezione di Bologna, CNR, Bologna, Italy.**

The focus of this study is on the adsorption properties of the nanocrystalline material and SnO<sub>2</sub> has been chosen as the appropriate example. Nanocrystalline SnO<sub>2</sub>, 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 a deeper understanding of its gas-absorbing properties in order to better exploit its gas-sensor applications. Therefore model structures consisting on small SnO<sub>2</sub> grains have been considered and the adsorbed system is generated by depositing a CO molecule above a tin or 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 Hartree-Fock and scattering theories. It has been found that the molecule is stably bonded to the grain without penetration or intermixing and adsorption is not dissociative. These are also properties of adsorption on the surfaces of bulk samples. However the analysis of the adsorbed system indicates that stable adsorption derives 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.

### **O3.16**

#### **Preparation of Pt-containing Intermetallic Nanoparticles via Sodium Naphthalide Reduction of Organometallic Precursors. Laif Robert Alden and Frank J. DiSalvo; Chemistry & Chemical Biology, Cornell University, Ithaca, New York.**

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 nanopowders. This work describes how such compounds can be prepared by chemical reduction of organometallic precursors by sodium naphthalide in tetrahydrofuran under argon atmosphere at room temperature. This reaction system can be employed to reproducibly prepare a nanopowder of PtPb and other intermetallics of interest, which are characterized by pXRD, SEM, STEM, EDS and CBED analyses. This synthesis also shows promise toward the development of generalizable methods for preparing intermetallic compounds as nanopowders due to the strong reducing ability of sodium naphthalide.

### **O3.17**

#### **TEM Size Distribution Study for Platinum Nanoparticles: Impact of Preparation Techniques.**

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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)maleonitrile and related poly(cyclodiborazane) derivatives were studied as potential substrates for the synthesis and encapsulation of platinum nanoparticles. The potential for oxidative addition versus dative bonding to the nanoparticles was modeled using the reaction between *bis*(methylthio)maleonitrile and *cis*- $(\eta^2\text{-C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2$  and monitored using <sup>1</sup>H 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. Since XRD is weighted by 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 are expected to yield the highest precision. The impact of TEM specimen preparation and nanoparticle encapsulation are expected to be key factors impacting the determination of particle size



distribution, and so, this became a focal point of the study. The TEM data collected revealed distributions that were compared with the results of XRD and EXAFS experiments. In this way, the relative merits 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.

### **O3.18**

**Nano-Plasmonic Building Blocks for Robust Nanoscale Devices.** Sudhaprasanna Kumar Padigi<sup>1</sup>, Jorge Quijano<sup>1</sup> and Shalini Prasad<sup>1,2</sup>; <sup>1</sup>Electrical and Computer Engineering, Portland State University, Portland, Oregon; <sup>2</sup>Bio-medical Engineering, Oregon Graduate institute, Hillsboro, Oregon.

A platform based technique for amplifying signals from micro and nano-scale devices used for monitoring applications has been developed. It comprises of dielectric substrate (SiO<sub>2</sub>) 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 voltage levels, leading to better S/N ratio, making 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**

### **O3.20**

**Design and Integration of Sensing Arrays with Nanoparticle Thin Films as Sensing Materials.** Mark J Schadt, William Cheung, Hyein Koh, Jin Luo, Kaylie Young and Chuan-Jian Zhong; Chemistry, State University of New York at Binghamton, Binghamton, New York.

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 nanostructure, 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 capping ligands, the assembly of the nanoparticles into thin films with linking ligands, the construction of micro-electrode arrays, and the design and optimization of circuit board hardware for organic vapor sensing measurements. The syntheses 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 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. Efimov<sup>1</sup>, Alexei A. Volodin<sup>1</sup>, Pavel V.

Fursikov<sup>1</sup>, Boris P. Tarasov<sup>1</sup>, Yurii M. Shulga<sup>1</sup>, Igor I. Khodos<sup>2</sup> and Yusif A. Kasumov<sup>2</sup>; <sup>1</sup>Institute of Problems of Chemical Physics, Chernogolovka, Russian Federation; <sup>2</sup>Institute 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 photolithographic 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

supported Fe-Mo-S catalyst first prepared using a solution of a heterometallic carbonyl-chalcogenide complex containing Fe and Mo[4]. to synthesize carbon nanotubes and nanofibers by pyrolysis of methane and hydrogen gas mixture at 900 C. The structure of carbonaceous products as well as metal nanoparticles was studied by TEM, SEM, electron microprobe analysis and Auger electron spectroscopy. Procedure of catalyst preparation allowed us to obtain nano-sized nanoparticles located on the surface of the support. During the pyrolysis metal particles stayed on the titanium nitride surface that shows to a specific role of the support. Nanofibers obtained during the pyrolysis have mainly bamboo-like structure. They demonstrate a roughly equal length of sections of a bamboo-fiber. This may evidence a certain periodicity in the process of nanofiber growth. We also notice the role of sulfur additives to the heterometallic catalyst in the process of nanofiber growth. The study was supported by the Russian Foundation for Basic Research (grant 2760). References. 1. Fursikov P.V., Tarasov B.P. International Scientific Journal for Alternative Energy and Ecology (ISJAE), 2004, N 10, P.5. 2. Khodos I.I., Tarasov B.P., Kasumov Yu.A., et al. Proceedings of 7-th International Conference on Nanostructured Materials. 2004, Wiesbaden/Germany. (NANO 2004), P.56. 3. Harutyunyan A.R., Pradhan B.K., Kirn U.J., et al. Nanoletters, 2002, Vol.2, N 5. P.525. 4. Pasynskii A. A., Dobrokhotova Zh. V., Torubaev Yu. V., et al. Russian Chemical Bulletin. 2003.Vol.52. P.109.

### **O3.22**

**Fabrication and Characterization of Molybdenum Oxide Nanofibers/ Nanowhiskers by Electrospinning.** Guan Wang, Katarzyna Sawicka, Yuan Ji, Xianrong Huang, Michael Dudley and Pelagia-Irene Gouma; 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 electrosinning technique. By calcination of the composite fibers, pure molybdenum oxide 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 EDX and grazing incidence XRD. Calcination process was studied by DSC and TG analysis. The results showed that crystallinity of the metal oxide nanofibers depended on the calcination temperature.

### **O3.23**

**Synthesis of 2D and 3D Metal Nanoarrays and Semiconductor Nanoparticles in Supercritical Fluid Carbon Dioxide.** Carlos Alberto Fernandez, 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-CO<sub>2</sub> microemulsions, respectively. Chemical reduction of metal ions (e.g., Au<sup>3+</sup>) 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 Cd<sup>2+</sup> and the other containing S<sup>2-</sup>, 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 CO<sub>2</sub> is tunable by varying temperature and pressure, we are developing techniques for synthesizing metal and semiconductor nanoparticles of controllable sizes using water-in-CO<sub>2</sub> microemulsions as templates. The synthesized nanoparticles can be stabilized using an alkanethiol compound. Self-assembling 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 described.

### **O3.24**

**Metal Wires Encapsulated within TiO<sub>2</sub> Nanotubes.** Bryan M. Rabatic<sup>1</sup>, Zoran V. Saponjic<sup>2</sup> and Tijana Rajh<sup>2,1</sup>; <sup>1</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Chemistry Division, Argonne National Laboratory, Argonne, Illinois.

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

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 generate binary inorganic 1D nanostructures consisting of a scrolled tube of the semiconductor TiO<sub>2</sub> encapsulating a nanowire of Ag metal within its central core. Previously, we have shown that the undercoordinate character of Ti atoms present upon the tube surface leads enhances chemical reactivity. This unique characteristic is used to assist 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 amphiphilic molecule (L-ascorbic acid 6-palmitate) to the surface of the TiO<sub>2</sub> tubes is sufficient to act as this phase transfer agent. Upon binding of the amphiphilic molecule to TiO<sub>2</sub>, dispersion of the inorganic/organic hybrid from water into hexane is possible. As this occurs, water becomes trapped within the interior (hydrophilic) region of the TiO<sub>2</sub>. To this, we use mixed phase agitation to deliver silver ions to the central core of the nanotube. After penetration of ions into the hydrophilic core, light is used to induce the reduction of the ions into silver metal resulting in a nanowire confined to the interior core of the TiO<sub>2</sub> 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.** Gang Wang and Siu-Tung Yau; Physics, Hunter College of City University of New York, New York, New York.

Glucose oxidase (GOx) was immobilized on unmodified edge 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 all 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 mA/mM and a detection limit of 50 mM.

### **O3.26**

**Nanofabrications and Microfluidic Synthesis of Bio-materials for Sensor or Catalyst Applications.** Lisa S. Brown, University of California, Irvine, Irvine, California.

Micro- or nano-fabrication offers us numerous active devices by patterning small features on a variety of substrates to meet a set 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 the controlled addition of reagents and their rapid and efficient mixing in picoliter volumes. Following reagent droplet formation, the microfluidic channel design results in exclusive fusion of alternate droplets with concomitant rapid mixing of their contents to produce a supersaturated solution of Cd<sup>2+</sup> and S<sup>2-</sup> 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 determined by X-ray and electron diffractions, respectively. They are typically tens of micrometers in length and few 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 grown by many other methods, despite 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 above band gap photons, 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<sub>2</sub> and H<sub>2</sub>S resulted in stronger luminescence, but exposure to CO, O<sub>2</sub> and air in weaker luminescence. Exposure to inert gases, such as Ar and N<sub>2</sub>, 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 luminescent intensity 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 of electron-hole pairs, which affects the NBE luminescence intensity. The model is supported by the observations that (a) below band gap excitation of the nanowires does not induce a response when the nanowires are exposed to the gases, and (b) 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, K.M. Ip, 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 partially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 401003) and a CUHK direct grant (Project code 2060277).

### **O3.28**

**Characterization of Ceria Nanoparticles Prepared by Various Synthetic Methods.** Seog-Jin Jeon<sup>1</sup>, Seung-Man Yang<sup>1</sup>, Jae-Hyun So<sup>2</sup> and Dong-Jun Lee<sup>1</sup>; <sup>1</sup>Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, DaeJeon, South Korea; <sup>2</sup>Korean Intellectual Property Office, DaeJeon, South Korea.

Outstanding physical and chemical properties of ceria nanoparticles such as oxygen storage capacity and high stiffness have attracted 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 NO<sub>x</sub> 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, physicochemical 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 routes will be 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, crystallite size and lattice parameters 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<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> on ceramic foams for phthalic anhydride catalysis.** Heiko Schulz<sup>1</sup>, Bjoern Schimmoeller<sup>1</sup>, Sotiris E. Pratsinis<sup>1</sup>, Anika Bareiss<sup>2</sup>, Andreas Reitzmann<sup>2</sup> and Bettina Kraushaar-Czarnetzki<sup>2</sup>; <sup>1</sup>Department for Mechanical and Process Engineering, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland; <sup>2</sup>Department for Chemical and Process Engineering, University of Karlsruhe, Karlsruhe, Germany.

The partial oxidation of *o*-xylene to phthalic anhydride is a highly exothermic reaction. The evolving heat has to be transferred effectively out of the catalyst bed, because hot spots deactivate the catalyst irreversibly and lead to an increased risk of thermal reactor runaway. Ceramic foams of Al<sub>2</sub>O<sub>3</sub> can improve the 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 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 crucial for high activity but 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 23 - 120 m<sup>2</sup>/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 supports 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 nitrogen adsorption, 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.

### O3.30

#### Chemical bath deposition of nanocrystalline CdS and CdPbS layers and investigation of their photoconductivity.

Vilmos Rakovics, Optoelectronic Devices, MTA MFA, Budapest, Hungary.

CdS films were grown onto glass and InP substrates by chemical bath deposition (CBD) technique. Results on structural, 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<sup>2+</sup> doped layers. Addition of Pb<sup>2+</sup> result layered 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 In<sub>2</sub>S<sub>3</sub> epitaxial layer at the InP/CdS interface. Photosensitivity increases and carrier life time decreases as a result of Cu addition into a bath, or post annealing of CdS layers in CuCl<sub>2</sub> 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.

Crystallographic orientation of atomic planes makes a metal amenable to specific properties as desired in catalysis and environment sensing. Oriented metal nanoparticles are however less known. Here we present x-ray diffraction, transmission electron microscopy and atomic force microscopy data to provide evidence of copper nanoparticles with preferred orientation, achieved by electro explosion of copper wires in an aqueous medium [1]. The optical absorption in these particles is devoid of the usual Mie resonance at 580 nm for Cu nanoparticles, while maintaining bulk-like lattice periodicity [2]. Under highest reorientation (largest orientation index), absorption in ultraviolet region is characterized by distinct and sharp resonant peaks, which correlate with occupied valence band density of state (DOS) from copper clusters [3], making these truly crystalline particles with atom-like electronic properties. References: [1] Sen P., Ghosh J., Abdullah A., Kumar P. and Vandana, Proc. Indian Acad. Sci. Chem. Sci.115 (2003) 499. [2] Om Parkash, Sen P. and Sarma A. (paper under review, 2005) [3] Eberhardt W., Surface Science 500 (2002) 242.

### O3.32

#### Surface-Tailored CdSe Quantum Dots/Polymer Composite Films for the Selective and Sensitive Detection of Hydrocarbons.

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CdSe quantum dots (QDs) capped with trioctylphosphine 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 of the QDs into a polymer matrix for fluorescence based hydrocarbon (HC) 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 fluorinated aromatic and polyarene functionalized sensing groups attached to the QD surface, enhanced the interaction between the QDs and the targeted HC molecules, resulting in a 15ppm sensitivity towards xylenes in air, which is about 3 times the 50ppm sensitivity measured for toluene in air. During the HC 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 higher HC concentration levels. 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. Details concerning the design of tailored sensing ligands for the sensitive and selective detection of HCs, mechanism behind the fluorescence enhancement/quenching process as well as methods for increasing the nanocomposite sensing stability will be discussed.

### O3.33

#### Enhanced gas selectivity in nanostructured Gd<sub>1-x</sub>B<sub>x</sub>CoO<sub>3</sub> (B = Ba, Sr) prepared by solution method. Carlos R. Michel, Edgar Rene Lopez, Abraham Quino-Mendoza, Hector Guillen-Bonilla and Gloria Santillan-Dominguez; Physics, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

Oxides possessing the perovskite-type structure (ABO<sub>3</sub>), with cobalt in the B-site, exhibit outstanding transport properties and chemical activity, which make 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 GdCoO<sub>3</sub>, and members of the solid solutions Gd<sub>1-x</sub>B<sub>x</sub>CoO<sub>3</sub> and Gd<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>, by a solution 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 can be produced for barium and strontium-doped oxides, after a controlled annealing process; whereas micron-sized powders were produced for GdCoO<sub>3</sub>. To test these materials as environmental gas sensors, electrical measurements were made on sintered thick films of GdCoO<sub>3</sub>, Gd<sub>0.9</sub>Ba<sub>0.1</sub>CoO<sub>3</sub> and Gd<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub>, in air and CO<sub>2</sub>. 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 GdCoO<sub>3</sub>, reached its maximum sensitivity to CO<sub>2</sub> 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 420°C, revealed that nanostructured Gd<sub>0.9</sub>Sr<sub>0.1</sub>CoO<sub>3</sub> and Gd<sub>0.9</sub>Ba<sub>0.1</sub>CoO<sub>3</sub> have good selectivity to this gas, whereas micron-sized GdCoO<sub>3</sub> did not show noticeable selectivity.

### O3.34

#### Core-Satellite Nanoassemblies with Designed Plasmonic Properties Controlled by DNA Hybridization.

David S. Sebban<sup>1</sup>, Thomas H. LaBean<sup>2</sup> and Anne A. Lazarides<sup>1</sup>; <sup>1</sup>Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; <sup>2</sup>Computer Science, Duke University, Durham, North Carolina.

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 satellite particles tethered to a larger core particle. In these assemblies, tether length is a function of the hybridization state of the DNA, and therefore controllable by addition of complementary DNA. Previously, we have shown that interparticle separations in extended networks of particles linked by duplex DNA are well-controlled, while separations between particles linked by single-stranded DNA are highly variable. Through intelligent choice of particle sizes and tether length, core-satellite 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 3'- or 5' disulfide-modified oligonucleotides and synthetic DNA linkers. 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.

### **O3.35**

**Cationic Lipid Modulates Phospholipid Adsorption on Silica.** Sergio P. Moura and Ana M. Carmona-Ribeiro; Departamento de Bioquímica, Instituto de Química 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) for a 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. Composite 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. Therefore, from M, it was possible to modulate DPPC adsorption aiming at bilayer deposition. All other data consistently pointed to improved colloid stability upon silica coverage with DODAB/DPPC bilayer. 1.Rapuno, R.; Carmona-Ribeiro, A. M. J. Colloid Interface Sci. 2000, 226, 299. 2.Moura, S.P; Carmona-Ribeiro, A.M. Langmuir 2003, 19, 6664. 3.Moura, S.P; Carmona-Ribeiro, A.M. Langmuir 2005, in press. 4.Moura, S.P; Carmona-Ribeiro, A.M. Cell Biochemistry and Biophysics 2005, in press Financial Support: FAPESP and CNPq

### **O3.36**

**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, the mechanical properties 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 studied and will be discussed.

### **O3.37**

**Texture formation and optical response in thin liquid crystal film on patterned surface.** Dae-Kun 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 advantages of this biosensor and potential uses, the 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 involved, 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 texture under cross polar is computed 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 and 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.

### **O3.38**

**Biofunctional Probes Built on Carbon Nanotube Scaffolds.** Evan Goulet and David E. Luzzi; Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania.

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 colloidal silica network produced 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.

### **O3.39**

**Flame 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 photosplitting of water using solar energy is a potentially clean and renewable source of hydrogen fuel that is environmentally benign and easily distributed. Light impacting titanium dioxide electrodes immersed in water causes the water to split into oxygen and hydrogen. However, pure bulk TiO<sub>2</sub> 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 hole 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 water splitting, 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 unsintered primary particles. These films had the lowest roughness and the lowest 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 flowrate drastically decreased 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 activity 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

**Amplified Quenching of Poly(phenylene ethynylene) Thin Films in Aqueous Environment for Biosensing Applications.** Jessica H. Liao<sup>1,2</sup>, Lars Geiger<sup>2</sup>, Guy D. Joly<sup>2</sup>, Jordan H. Wosnick<sup>2</sup> and Timothy M. Swager<sup>2</sup>; <sup>1</sup>Department of Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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 in biodetection strategies. The three-dimensionality afforded from thin films of non-aggregating poly(phenylene ethynylene)s (PPE)s allows for favorable  $\pi$ - $\pi$  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, the nature of van der Waals forces in an aqueous environment 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 and sensitivity in biological environments. We are currently working towards the implementation of PPE films as transducers for detecting proteases relevant to biomedical research and with this demonstration gain a fundamental understanding of electron transfer fluorescence quenching in aqueous environments.

#### SESSION O4: Catalysis II

Chairs: Valeri Petkov and Chuan-Jian Zhong

Tuesday Morning, November 29, 2005

Room 200 (Hynes)

### 8:15 AM O4.1

**Theory of Carbon Monoxide on Cobalt Nanoparticles: Size Dependence of Binding Energies, Magnetism and Catalysis.** Fernando Agustin Reboredo, Physics and Advanced Technologies, Lawrence Livermore National Laboratory, Livermore, California.

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 transitions as a function of 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 H<sub>2</sub> 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 or icosahedral), 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

**Materials Advances for Fuel Cell Applications.**

Hector D. Abruna, Department of Chemistry & Chemical Biology, Cornell University, Ithaca, New York.

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

**Catalytic Activity of Gold Nanoparticles on Titanium Oxide: The Effects of Size, Shape, and Oxide Structure.**

Sergey Rashkev<sup>1,2</sup>, Andrew R. Lupini<sup>1</sup>, Alberto Franceschetti<sup>2,1</sup>, Bei Chen<sup>3</sup>, Wenfu Yan<sup>3</sup>, David R. Mullins<sup>3</sup>, Viviane Schwartz<sup>3</sup>, Sheng Dai<sup>3</sup>, Yiping Peng<sup>1</sup>, Sokrates T. Pantelides<sup>2,1</sup>, Steven H. Overbury<sup>3</sup> and Stephen J. Pennycook<sup>1,2</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Lab, Oak Ridge, Tennessee; <sup>2</sup>Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; <sup>3</sup>Chemistry Sciences Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

Nano-sized gold clusters or very thin gold layers on a titanium 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 sized gold particles, 1-2 atomic layers thick, on nanocrystalline titanium oxide demonstrate high catalytic activity, and the catalytic activity drops down when the size of the particle 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 defined 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 only on the number of oxygen vacancies on the oxide surface to which the gold atoms of the cluster bind. Reactive undercoordinated titanium atoms positioned 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

**Platinum Nanoparticle Encapsulation by Hydrothermal Synthesis of Mesoporous Oxides: Synthesis, Characterization and Catalytic Properties.** Robert M. Rioux<sup>1,2</sup>, Krisztian Niesz<sup>1,2</sup>, Susan E. Habas<sup>1,2</sup>, Michael E. Grass<sup>1,2</sup>, Hyunjoon Song<sup>1,2</sup>, Peidong Yang<sup>1,2</sup> and Gabor A. Somorjai<sup>1,2</sup>; <sup>1</sup>Chemistry, University of California, Berkeley, Berkeley, California; <sup>2</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

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 shapes were 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 cubes, cuboctahedra 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 displace 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 cyclohexene 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 products (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  $\alpha,\beta$  unsaturated aldehyde.

Experimental observations have shown that larger Pt particles are more selective for formation of the unsaturated alcohol. This study emphasizes all three aspects of catalyst design: synthesis, 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 O4.5

**Quantitative Study of Au and Pt Catalytic Clusters by STEM and HRTEM.** Fengting Xu<sup>1</sup>, Laurent Menard<sup>2</sup>, Huiping Xu<sup>1</sup>, Shangpeng Gao<sup>1</sup>, Lin-Lin Wang<sup>3</sup>, Anatoly Frenkel<sup>4</sup>, Ralph Nuzzo<sup>2</sup>, Duane D. Johnson<sup>3</sup> and Judith C. Yang<sup>1</sup>; <sup>1</sup>Department of Materials Science & Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania; <sup>2</sup>Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>3</sup>Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; <sup>4</sup>Department 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 cluster's 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 their 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 mrad) annular dark-field, HAADF) 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 Re<sub>6</sub> and PtRu<sub>5</sub> clusters [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 g-Al<sub>2</sub>O<sub>3</sub> supported Pt clusters are performed. We are able 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, *Microsc. Microanal.*, **6**, 353 (2000). [3] J.C. Yang, 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 O4.6

**Three-Dimensional Structure of Metallic Nanoparticles from High-Energy X-ray Diffraction and Atomic Pair Distribution Function Analysis.** Valeri Petkov, 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, materials constructed at the nanoscale, such as nanoparticles, lack the translational symmetry and long-range order of usual crystals. The diffraction patterns of such materials show only 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 0304391(NIRT).

#### 10:30 AM \*O4.7

**Enhanced Charge Transport in Oxide Nanoarchitectures via Bonded Electrical Pathways.** Debra R. Rolison<sup>1</sup>, Michael S. Doescher<sup>1</sup>, Christel Laberty-Robert<sup>2,1</sup>, Jeffrey W. Long<sup>1</sup>, Jeremy J. Pietron<sup>1</sup>, Charles A. Edmondson<sup>3</sup>, Katherine A. Pettigrew<sup>1,4</sup> and Rhonda M. Stroud<sup>4</sup>; <sup>1</sup>Surface Chemistry, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>CNRS-UMR 5085, Université Paul Sabatier, Toulouse, Cedex 04, France; <sup>3</sup>Physics Department, U.S. Naval Academy, Annapolis, Maryland; <sup>4</sup>Sensors 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 ambigels, which are sol-gel-derived ultraporos nanoarchitectures, unite high surface area 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 that of the same material expressed as crystalline nanoparticles. In MnO<sub>2</sub> ambigels 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 MnO<sub>2</sub>. Alternatively, grinding the ambigel 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 ambigels exhibit higher oxygen-ion conductivity and more rapid spectral response to changes in the partial pressure of oxygen relative to nanocrystalline CeO<sub>2</sub>. 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* **299** (2003) 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 O4.8

**Density Functional Theory Modeling of Bimetallic Nanoclusters for PEM Fuel-Cell Cathode Electrocatalysis.** Liang Qi<sup>1</sup>, Xiaofeng Qian<sup>2</sup>, Clemens J. Foerst<sup>2</sup>, Jianguo Yu<sup>1</sup>, Sidney Yip<sup>2</sup> and Ju Li<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio; <sup>2</sup>Department 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 quasiatomic minimal basis orbital (QUAMBO) 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 O4.9

**In Situ Synchrotron X-Ray Studies of CO Oxidation By Au/TiO<sub>2</sub>.** Dillon Fong<sup>1,2</sup>, J. A. Eastman<sup>1</sup>, P. H. Fuoss<sup>1</sup>, G. W. Zhou<sup>1</sup>, P. M. Baldo<sup>1</sup> and L. J. Thompson<sup>1</sup>; <sup>1</sup>Materials Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois.

While bulk Au is inert, Au particles approximately three nanometers in diameter are highly efficient at converting CO to CO<sub>2</sub> even at room temperature (1). Diameter is not the only important dimensional variable: ultrathin Au films on TiO<sub>x</sub> also catalyze CO oxidation, and it has been found that a 4/3-monolayer Au thickness exhibits maximum 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 NO<sub>x</sub> 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<sup>-7</sup> 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-O<sub>2</sub>-Au reactions. The Au structure and strain state are varied by using either TiO<sub>2</sub>(110) or TiO<sub>2</sub>-terminated SrTiO<sub>2</sub>(001) single-crystal supports. Reaction products are detected with a residual gas analyzer, and a substrate heater allows both the growth and reactions to be carried out at temperatures ranging 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* **306**, 252 (2004). 3. R. Meyer, C. Lemire, S.

**11:30 AM O4.10**

**Reduction in Size of PtRu Catalyst by Addition of Non-Metallic Elements and Improvement in Power Density of Direct Methanol Fuel Cell.** Hideo Daimon and Yukiko Kurobe; Development & Technology Division, Hitachi Maxell Ltd., Tsukuba-gun, Ibaraki, Japan.

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 buried 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 298 K with fuels of 15 wt.% methanol and ambient air. Loading amount of catalyst was 5 mg/cm<sup>2</sup> 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 P with Pt is higher than that of Pt with Pt, which suggests that Pt-Pt metallic bonding is cut by P. Cutting of metallic 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/cm<sup>2</sup> to 64 mW/cm<sup>2</sup> by utilizing 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 m<sup>2</sup>/g, 254 m<sup>2</sup>/g and 140 m<sup>2</sup>/g, respectively. TEM observation showed that size of these PtRuP catalysts is retained in 2 nm. Maximum power density of DMFC was improved by usage of 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.

**11:45 AM O4.11**

**Surface Properties of Supported Gold and Alloy Nanoparticle Catalysts.** Jin Luo, Mathew M. Maye, Nancy N. Kariuki, Lingyan Wang, Peter N. Njoki, Derrick Mott, Yan Lin, Mark Schadt, I-Im Stephanie Lim and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

We have recently been investigating core-shell assembled gold and alloy nanoparticle catalysts for electrocatalytic oxidation of carbon monoxide and methanol and reduction of oxygen, which are of interest to the development of fuel cell catalysts. The exploitation of the catalytic activity of such materials requires the ability to manipulate the interparticle spatial and surface properties in controllable ways. This ability is inherently linked to the controllable activation of the nanostructure in terms of nanocrystal size and surface properties. This paper reports recent findings of our investigations in probing the structural and morphological evolution of molecularly-capped gold and alloy nanoparticles on different support materials under thermal treatment using atomic force microscopy, infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The results have demonstrated that the nanocrystalline properties and surface binding sites can be fine tuned by a combination of factors including composition, calcination, adhesion, mobility, surface activation and surface tension. These findings have important implications to the design and processing of nanostructured catalysts.

SESSION O5: Chemical Sensor I  
Chairs: Jay Grate and F. P. Zamborini  
Tuesday Afternoon, November 29, 2005  
Room 200 (Hynes)

**1:30 PM O5.1**

**Vapor and Gas Sensing with Micro- and Nano-scale Films of**

**Monolayer Protected Clusters.** Frank Zamborini<sup>1</sup> and Francisco Ibanez<sup>2</sup>; <sup>1</sup>University of Louisville, Louisville, Kentucky; <sup>2</sup>Chemistry, 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 hexanethiolate coated gold monolayer protected clusters (C6 Au MPCs). The C6 Au MPCs were stamped into parallel lines (~1.2 μm wide and 400 nm tall) across two Au electrodes separated by a 1 μm gap. The chemiresistive vapor sensing properties were measured for saturated toluene and isopropanol vapors. As-prepared 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 hexanedithiol greatly improves their stability and leads to reversible responses. The extent of Au MPC cross-linking varies with different exposure times to dithiol 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 between 250 to 320 °C, 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 varies 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.

**1:45 PM \*O5.2**

**Monolayer-Protected Nanoparticles as Sorptive Phases for Sensing and Separations.** Jay W. Grate<sup>1</sup>, Marvin G. Warner<sup>1</sup>, David A. Nelson<sup>1</sup>, Skaggs Rhonda<sup>1</sup>, Robert E. Synovec<sup>2</sup> and Gwen M. Gross<sup>2</sup>; <sup>1</sup>Chemistry Division, Pacific Northwest National Laboratory, Richland, Washington; <sup>2</sup>Department of Chemistry, University of Washington, Seattle, Washington.

Adsorptive and absorptive 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 materials in these applications. Such materials can offer many potential advantages such as increased surface areas, exceptional volume densities of functional groups, and assembly into structures with nanometer linear dimensions from one feature to another. In this paper, we examine the use of monolayer protected gold nanoparticles as sorptive layers for chemical vapor sensor and gas 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.

**2:15 PM O5.3**

**Tin-Doped Hematite Nanoparticles for Gas Sensing Applications.** Monica Sorescu<sup>1</sup>, Lucian C. Diamandescu<sup>1,2</sup> and Doina Mihaila-Tarabasanu<sup>2</sup>; <sup>1</sup>Physics, Duquesne University, Pittsburgh, Pennsylvania; <sup>2</sup>Materials Science, National Institute for Materials Physics, Bucharest, Romania.

The (1-x)α-Fe<sub>2</sub>O<sub>3</sub>-xSnO<sub>2</sub> 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 were 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 refinements of the XRD spectra at low tin concentration are consistent with the presence of Sn<sup>4+</sup> in the α-Fe<sub>2</sub>O<sub>3</sub> structure in two different sites: substituting for Fe<sup>3+</sup> 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 SnO<sub>2</sub> structure crystallizes, where the Fe<sup>3+</sup> ions partially substitute for Sn<sup>4+</sup> ions in the structure. A phase separation of α-Fe<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> was observed for x>0.4: the α-Fe<sub>2</sub>O<sub>3</sub> structure containing tin decreases simultaneously with the increase of the SnO<sub>2</sub> 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 Fe<sup>3+</sup> in the vicinity of Sn<sup>4+</sup> nearest neighbors. The 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 Sn<sup>4+</sup> in the alpha-Fe<sub>2</sub>O<sub>3</sub> and x>0.7 for Fe<sup>3+</sup> in SnO<sub>2</sub>. This work is the first report on the hydrothermal synthesis and microstructure characterization of (1-x)alpha-Fe<sub>2</sub>O<sub>3</sub>-xSnO<sub>2</sub> system over the full range of tin concentration, from x=0.0 to x=1.0. Moreover, this synthesis route allowed us to reach nanometric particle dimensions, which would make the materials very important for gas sensing applications.

### 3:30 PM O5.4

**Towards Photonic Crystal-based Spectroscopic Gas Sensors.** Torsten M. Geppert<sup>1,2</sup>, Daniel Pergande<sup>2</sup>, Andreas von Rhein<sup>2</sup>, Stefan L. Schweizer<sup>2</sup> and Ralf B. Wehrspohn<sup>2</sup>; <sup>1</sup>Ordered Porous Materials/Photonic Crystals, Max Planck Institute of Microstructure Physics, Halle (Saale), Germany; <sup>2</sup>Dept. Physics, Nanophotonic Materials, University Paderborn, Paderborn, Germany.

Gas sensors are important in a broad range of technical fields such as environmental monitoring, medical, safety and security applications. The outstanding property of spectroscopic gas sensors compared to other types is their selectivity resulting from the IR "fingerprints" of common gases. However, a drawback of such optical systems is their relatively large size caused by the necessary size of the interaction volume of the dilute gaseous medium and the light. The use of photonic crystals (PhCs), e.g., made of macroporous silicon, allows a dramatic decrease in size of the interaction volume exploiting the very low group velocity  $v_g$  for flat bands in the photonic band structure. From FDTD and FEM simulations an absorption enhancement of more than 30 compared to a conventional interaction volume, e.g., a glass tube, was derived. However, a low  $v_g$  corresponds to a high effective refractive index and aggravates coupling of incoming light to these flat PhC Bloch modes, resulting in low transmission and therefore an unfavorable signal-to-noise-ratio. Investigations of different strategies to improve the transmission led to the development of a novel taper concept, the so-called Anti-Reflection-Layer (ARL) resulting in a transmission of more than 90% even for flat bands with low  $v_g$ . Its working principle is different from classical anti-reflection-coatings and based on a combination of surface diffraction at the ARL/PhC interface, surface modes in the ARL, total internal reflection at the air/ARL interface and mode-matching of the incoming plane wave and the Bloch-modes in the PhC. In addition, numerical simulations show that PhC-based gas sensors allow easy fine-tuning and are robust concerning non-perpendicular incidence of incoming light. Structures appropriate to be used for PhC based gas sensors including the ARL concept have been realized by a modification of the macroporous Si fabrication technique. This method allows realization of wafer-scale, ordered pore arrays with aspect ratios  $> 100$  (~450  $\mu\text{m}$  deep pores with ~3  $\mu\text{m}$  diameter) with simultaneous realization of the ARL concept. Optical characterization of these structures proof the enhancement of coupling light to flat PhC modes.

### 3:45 PM \*O5.5

**Chemical Sensing Using Metal Nanowires Prepared by Electrochemical Step Edge Decoration.** Reginald M. Penner, Department of Chemistry, University of California, Irvine, Irvine, California.

Previously we have demonstrated that polycrystalline noble metal nanowires may be electrodeposited by exploiting millimeter-long step edges on graphite surfaces to promote the nucleation of metal at the onset of nanowire growth. After the application of a nucleation voltage pulse, a linear ensemble of metal nanoparticles is formed along each step edge on the graphite surface and these nanoparticles are then grown until coalescence is achieved and a continuous nanowire is formed. This strategy for obtaining nanowires leads to ultra-long wires that are upwards of a millimeter in length, and these nanowires – like the step edges themselves – are organized into parallel arrays on the graphite surface, but the minimum nanowire diameter is 90 nm. This is the diameter at which significant size effects in noble metals nanowires begin to be observed, and this fact provides a motivation for devising methods for synthesizing smaller wires. In this talk, we begin by describing two refinements of this electrochemical step edge decoration (ESED) technique that permits nanowires with diameters down to 20 nm, to be prepared. One technological application for such nanowires is chemical sensing. Progress in this direction will be summarized in this talk. I focus attention on experiments in which a resistance change for an ensemble of metal nanowires is induced by the chemisorption of molecules. Several types of sensors, analyte species, and sensing mechanisms, will be discussed.

### 4:15 PM O5.6

**Doping Control and Transient Responses in Single Nanotube Nanofluidic Transistors.** Rong Fan<sup>1</sup>, Min Yue<sup>2</sup>, Rohit Karnik<sup>2</sup>, Arun Majumdar<sup>2</sup> and Peidong Yang<sup>1</sup>; <sup>1</sup>Department of Chemistry, University of California at Berkeley, Berkeley, California; <sup>2</sup>Mechanical Engineering, University of California at Berkeley, Berkeley, California.

The ability to manipulate charge carriers (electrons and holes) in

metal-oxide-semiconductor field effect transistors (MOSFETs) has revolutionized how information is processed and stored, and created the modern digital age. Analogous to MOSFETs, introducing field effect modulation in micro/nanofluidic 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 (MOSofETs) 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 interests in this gapless transport system. Possion-Boltzmann model is employed to extract two key physical parameters – zeta potential and surface charge density – based on experimental measurements. Moreover, transient study was carried out, leading to the first kinetic model of field effect in ionic solutions. Nanofluidic FETs promote nanofluidics to a higher level of controllability or even logic, and have potential implications in sub-femtoliter analytical techniques and the integration of large-scale nanofluidic circuits.

### 4:30 PM O5.7

**Towards Understanding of Metal Oxide Nanowire Conductometric Sensors: Spectromicroscopy Approach.** Andrei A. Kolmakov<sup>1</sup>, Stephen Jesse<sup>2</sup>, Uday Lanke<sup>1</sup>, Yigal Lilach<sup>3</sup>, Sergei V Kalinin<sup>2</sup> and Arthur P Baddorf<sup>2</sup>; <sup>1</sup>Physics, SIUC, Carbondale, Illinois; <sup>2</sup>ORNL, Oak Ridge, Tennessee; <sup>3</sup>PNNL, Richland, Washington; <sup>4</sup>CLS, Saskatoon, Saskatchewan, Canada.

To address the interplay between surface properties and electron transport in metal oxide nanowire sensors we have applied an array of imaging techniques based of electron and scanning probe microscopies. In particular, using Synchrotron Radiation based X-PEEM imaging of the wired nanostructure we were able to acquire the NEXAFS spectra from the surface of individual TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> nanowires thus opening a new avenue to visualize and spectroscopically 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 nanostructure. The particularities of the electron transport in the realistic device were studied as a function of gate potential and in presence of contact effects.

### 4:45 PM O5.8

**Macroscopic Fibbers of Oriented Vanadium Oxide Nanoscopic Ribbons: Application toward High Sensitive Alcohol Micro-Sensor.** Renal Backov<sup>1</sup>, Lahire Biette<sup>1</sup>, Florent Carn<sup>1</sup>, Maryse Maugey<sup>1</sup>, Marie-France Achard<sup>1</sup>, Nathalie Steunou<sup>2</sup> and Jacques Livage<sup>2</sup>; <sup>1</sup>CRPP-CNRS/Universite Bordeaux-I, Pessac, France; <sup>2</sup>LCMC/ 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 biliquid foams) to design new macrocellular materials.[1-3] As discussed below the macroscopic thermodynamic pattern can be substituted by a shear process that allows reaching one dimensional (1D) materials. Among inorganic polymers, extensive interest is focused over 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 photochromism 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 nanotube 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 nanoscopic ribbons organized with a preferential orientation parallel to the macroscopic thread main axis. Those fibbers allow fast cycling insulator-semiconductor properties directly related respectively to the absence or presence of an alcohol vapor source, acting so as a highly sensitive and fast alcohol micro-sensor. For instance, they can detect down to 0.1 ppm of alcohol vapor within 16 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. Colin, M.-F. Achard, H. Deleuze, C. Sanchez, R. Backov Adv. Mater., 2005, 17, 62. 3- F. Carn, A. Colin, M.-F. Achard, H. Deleuze, R. Backov Adv. Mater., 2004, 6, 140. 4- L. Biette, F. Carn, M. Maugey, M.-F. Achard, N. Steunou, J. Livage, R. Backov Nature Materials (submitted).



### O6.1

**Structure Determination of Small Metal Clusters by Density-Functional Theory and Comparison with Experimental Far-Infrared Spectra.** Christian Ratsch<sup>1</sup>, Andre Fielicke<sup>2</sup>, Joerg Behler<sup>2</sup>, Matthias Scheffler<sup>2</sup>, Gert von Helden<sup>2</sup> and Gerard Meijer<sup>2</sup>; <sup>1</sup>Mathematics, UCLA, Los Angeles, California; <sup>2</sup>Fritz-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 nanoparticles 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 multiple photon dissociation. Using DFT calculations, we calculated the ground state energy and vibrational spectra for a large number of stable and unstable geometries of such 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 Monoclinic and Cubic Rare Earth Oxide Nanoparticles.** Ashley S Harvey<sup>1</sup>, Bing Guo<sup>2</sup>, Ian M. Kennedy<sup>2</sup>, Subhash H. Risbud<sup>1</sup> and Valerie J. Leppert<sup>3</sup>; <sup>1</sup>Chemical Engineering and Materials Science, University of California, Davis, California; <sup>2</sup>Mechanical and Aeronautical Engineering, University of California, Davis, California; <sup>3</sup>School 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 nano-phosphors for light emission and plasma displays. The acid-base chemistry, surface, and transport properties of REO-NPs lead to desirable catalytic qualities, 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 each phase in the 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.

### O6.3

**Observation of a Quadrupole Plasmon Mode for a Colloidal Solution of Gold Nanoprisms.** Jill Millstone, Sungho Park, Kevin L. Shuford, George C. Schatz and Chad A. Mirkin; Chemistry, Northwestern University and Institute for Nanotechnology, Evanston, Illinois.

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 single crystalline gold nanoprisms 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 nanoprism 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 a strong dipole resonance that are characteristic of these novel structures. The experimental optical spectra agree with discrete dipole approximation calculations that have been modeled from the dimensions of gold nanoprisms produced in this synthesis.

### O6.4

**Abstract Withdrawn**

### O6.5

**Novel Chamber Design for Arc Synthesis of Carbon Nanostructures.** Thomas Gennett<sup>1,2</sup>, Chaiwat Engrakul<sup>2</sup>, Kale Franz<sup>2</sup>, Jeffrey Alleman<sup>2</sup>, Philip Parilla<sup>2</sup>, Kim M. Jones<sup>2</sup>, Jeffrey Blackburn<sup>2</sup>, Katherine Gilbert<sup>2</sup>, Anne C. Dillon<sup>2</sup> and Michael J. Heben<sup>2</sup>; <sup>1</sup>Chemistry, Rochester Institute of Technology, Rochester, New York; <sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado.

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 by confining the arc-production graphite rods within a 75 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 1gram/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<sup>1</sup>, Hongyou Fan<sup>2,3</sup>, Michael J. O'Brian<sup>1</sup>, Kevin J. Malloy<sup>1</sup>, Gabriel P. Lopez<sup>3</sup>, Jeffrey Brinker<sup>2,3</sup>, Mansor Sheik-Bahae<sup>4</sup> and Thomas W. Sigmon<sup>1</sup>; <sup>1</sup>Center for High Tech Materials, University of New Mexico, Albuquerque, New Mexico; <sup>2</sup>Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; <sup>3</sup>Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; <sup>4</sup>Department 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 potential 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 allows metals to be structured and characterized on the nanometer scale and incorporated into dielectric films. For instance, direct synthesis 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 shift 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 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 results of the plasmon enhanced local fields occurring near the gold nanoparticles.

## O6.7

**An electrospun carbon black-polymer fiber-based gas sensor.** Yong Shin Kim<sup>1</sup>, Duck Gun Park<sup>1</sup>, Youn Tae Kim<sup>1</sup>, Seung-Chul Ha<sup>2</sup> and Byungwoo Park<sup>2</sup>; <sup>1</sup>Electronics and Telecommunication Research Institute, Daejeon, South Korea; <sup>2</sup>School 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 based on electrospinning for fabricating the carbon black-polymer composite sensors. When 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 electrospinning deposition time over a selected sensing area. These nanostructural features had 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.

## O6.8

**Hydrothermal preparation and photocatalysis of titanium dioxide.** Wen-Ren Li<sup>1</sup>, Yi-Fun Xie<sup>2</sup> and Chaochin Su<sup>2</sup>; <sup>1</sup>Department of Chemistry, National Central University, Zhongli City, Taoyuan County, Taiwan; <sup>2</sup>Institute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei, Taiwan.

Titanium dioxide (TiO<sub>2</sub>) is one of the most important semiconductors for photocatalytic application due to its strong oxidizing power of its holes, high photostability and redox selectivity. In particular anatase phase TiO<sub>2</sub> has been greatly studied due to its high photocatalytic activity in the decomposition of various organic pollutants in the environment. In this work, the pure anatase-phase TiO<sub>2</sub> nanocrystal was synthesized by a simple one pot experiment under hydrothermal condition. Titanium (IV) n-butoxide (Ti(O-Bu)<sub>4</sub>) was used as a precursor of TiO<sub>2</sub> and acetic acid (CH<sub>3</sub>COOH) was used as peptizer. The particle dimension and morphology of the product was examined by transmission electron microscopy (TEM), the crystal structure by X-ray diffraction (XRD), and chemical state was identified by electron spectroscopy for chemical analysis. The effect of hydrothermal parameters on the formation of anatase phase at different temperatures for various reaction times have been studied in detail. The photocatalytic activity of as-prepared TiO<sub>2</sub> was tested in the reaction of methylene blue (MB) photodegradation in aqueous solution. The results show strong correlation between the structure evolution, particle size, and photocatalytic performance of the TiO<sub>2</sub> samples to the hydrothermal treatment conditions. The anatase TiO<sub>2</sub> was successfully obtained at temperature as low as 150 °C. The anatase TiO<sub>2</sub> particles were 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 m<sup>2</sup>g<sup>-1</sup> with increase of hydrothermal treatment time up to 24 hours at 200 °C. To study the thermal stability of anatase TiO<sub>2</sub>, calcination experiment was carried out at higher temperatures. A phase transformation from anatase to rutile (A→R) was aroused at a calcination temperature of 700 °C and completed at 800 °C. The TiO<sub>2</sub> particles 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. Those results indicate that the anatase-phase dominated the MB decomposition under the experimental conditions. A plausible explanation correlating the photocatalytic activity and the TiO<sub>2</sub> preparation conditions is discussed.

## O6.9

**Active Pt Clusters from Dispersed Single Atoms on Carbon Nanotubes.** Yong-Tae Kim<sup>1</sup>, Kazuyoshi Ohshima<sup>1</sup>, Koichi Higashimine<sup>2</sup>, Kazuo Kato<sup>3</sup>, Tomoya Uruga<sup>3</sup>, Keiichi Osaka<sup>3</sup>, Kenichi Kato<sup>3,4</sup>, Masaki Takata<sup>3,4</sup>, Hiroyoshi Suematsu<sup>3</sup> and Tadaaki Mitani<sup>1</sup>; <sup>1</sup>School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan; <sup>2</sup>Center for Nano

Materials and Technology, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa, Japan; <sup>3</sup>Japan Synchrotron Radiation Research Institute /SPring-8, Mikazuki, Hyogo, Japan; <sup>4</sup>Core Research for Evolutional Science and Technology, Japan Science Technology Cooperation, Kawaguchi, Saitama, Japan.

The discoveries of carbon nanomaterials such as C<sub>60</sub> 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 redox reaction of the fuel gas or liquid on the electrocatalytic 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 conductivity. 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 electrochemical stability, and have shown a high electrocatalyst performance compared with carbon black. There have been limitations, however, to produce small size and monodispersion of electrocatalytic active materials on CNT. In order to improve the dispersity, chemical modifications have been attempted at the surfaces of carbon nanotubes using functional groups, such as carboxylic, carbonyl, 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 (H<sub>2</sub>PtCl<sub>6</sub>) with NaBH<sub>4</sub> 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 the reduction of a Pt precursor on thiolated multi-walled 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 agglomeration of single Pt atoms was started, and then reached a dynamically fluctuating state. Through slow quenching to R.T., monodispersed clusters, about 1 nm in size were formed. The monodispersed 1nm clusters showed the highest electrocatalytic activity for the methanol oxidation reaction. Moreover, our 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 coincidentally 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.

## O6.10

**Characterization of Cubic Mesoporous TiO<sub>2</sub> Thin Films by Spectroscopic Ellipsometric Porosimetry Technique.** Jean-Philippe Piel, A. Darragon, P. Heinrich, Y. Turcant and J. L. Stehle; SOPRA[1], Bois-Colombes, France.

Crystalline TiO<sub>2</sub> (Anatase configuration) thin films is 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 solvent using Sol-Gel processes. It allows the introduction of organic 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 calculated the volume of solvent adsorbed by the pores 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 gives 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 1nm in radius) using the Dubinin Radushkevitch formalism 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] SOPRA, 26 rue P. Joigneaux, 92270 Bois-Colombes, France

## O6.11

**Characterization of the surface of nanostructured zirconia-containing catalysts by ESR spectroscopy of O<sub>2</sub>-radical anions.** Natalya V. Mezentseva, Alexander F. Bedilo, Vladislav A. Sadykov and Alexander M. Volodin; Boreskov Institute

of Catalysis, Novosibirsk, Russian Federation.

Oxide materials on the basis of stabilized ZrO<sub>2</sub>-CeO<sub>2</sub> 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 two groups of materials:

(1) materials containing separate zirconia nanoparticles with typical size 1-3 nm localized between the aluminosilicate layers of natural clays; and (2) materials containing mesoscopic aggregates of ~5 nm zirconia nanoparticles. O<sub>2</sub>- radical anions generated by adsorption of hydrogen peroxide or NO+O<sub>2</sub> mixture were used as spin probes for characterization of the nanostructured zirconia-containing catalysts by ESR. The concentrations of oxygen radical anions formed by H<sub>2</sub>O<sub>2</sub> decomposition over zirconia pillared clays doped with different metal cations appeared to exceed those of monoclinic and cubic zirconia. Meanwhile, adsorption of the NO+O<sub>2</sub> mixture on clays stabilized by ZrO<sub>2</sub> nanoparticles did not lead to the appearance of O<sub>2</sub>- radicals. This result clearly indicates that the surface properties of ZrO<sub>2</sub> 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+O<sub>2</sub>. They are known to be formed in significant concentrations on zirconia samples having strong Lewis acid sites. Nanoscale ZrO<sub>2</sub> pillars apparently do not have such sites, and that is why oxygen radical anions are not formed from the NO+O<sub>2</sub> mixture on them. Comparison of the O<sub>2</sub>- formation from NO+O<sub>2</sub> over different crystalline modifications of ZrO<sub>2</sub> has shown that monoclinic zirconia has the highest specific concentration of surface sites where O<sub>2</sub>- radical anions are formed. This result agrees well with the observation that nitrosyl complexes are formed in highest concentrations over monoclinic zirconia having the most significant distortions in the coordination sphere of zirconium cations. Thus, both similarities and significant discrepancies have been observed in the relative concentrations 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 O<sub>2</sub>- radical anions. If liquid hydrogen peroxide is used, the O<sub>2</sub>- radical anions are formed via an acid-base reaction with participation of terminal hydroxyl groups, whereas nitrosyl complexes appear to be key intermediates in O<sub>2</sub>- generation from NO and O<sub>2</sub>. 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 oxide catalysts containing zirconium cations. This work is supported by Zamaraev International Charitable Scientific Foundation and Integration Project 8.23 of Presidium RAS.

#### **O6.12**

##### **Non-lithographic Nanofabrication Using Porous Alumina Membranes.** Bhargava Ram Kanchibotla<sup>1</sup>, Lu Tian<sup>2</sup> and Latika

Menon<sup>1</sup>; <sup>1</sup>Physics, Northeastern University, Boston, Massachusetts; <sup>2</sup>Physics, Texas Tech, Lubbock, Texas.

We have used a non-lithographic nanofabrication method for producing 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 a layer of as-deposited aluminum. The 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 pore 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

#### **O6.13**

##### **Effects of Ni Nanoparticles on Hydrogen Sensitivity of SnO<sub>2</sub>-based Gas Sensor.** Yuhua Xiong, Lei Wang, Jun Du and Xiuying Wei; General Research Institute for Nonferrous Metals, Beijing, China.

Tin dioxide films with nanocrystalline are the most promising materials for the development of gas sensor towards 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 SnO<sub>2</sub>-based gas sensors. In this paper, a SnO<sub>2</sub> 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 SnO<sub>2</sub>-based gas sensor were studied. Prior to and after different treatments including Ar<sup>+</sup> sputtering, vacuum annealing, and

heat treatment in oxygen environment for the SnO<sub>2</sub> films with and without modification, chemical composition and surface microstructure of these films were investigated by X-ray Photoelectron Spectroscopy (XPS) and Field-emitted scanning electron Microscopy (FESEM). The results show that the surface microscopy of SnO<sub>2</sub> films is greatly influenced by different treatment methods. FESEM observation shows nickel nanoparticles discontinuously distribute on the surface of Ni modified SnO<sub>2</sub> film or permeate into the SnO<sub>2</sub> 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. Chemically adsorbed oxygen sites will increase owing to the introduction of Ni<sup>2+</sup> compared with unmodified SnO<sub>2</sub> thin films. In addition, surface resistance of these films which is sensitive to chemisorption and reducing reactions is mainly controlled by the microstructure and chemical composition of the surface. Finally, the results indicate that the difference of gas-sensing properties of the Ni modified SnO<sub>2</sub> film and unmodified SnO<sub>2</sub> film is determined by their surface chemical composition and morphology. Compared with the unmodified SnO<sub>2</sub> film, the Ni surface modified SnO<sub>2</sub> film annealed in vacuum environment has the greatest sensitivity to 1000ppm hydrogen gas in dry air at relative 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 Kuncicky<sup>1</sup>, Steven D. Christesen<sup>2</sup> and Orlin D. Velev<sup>1</sup>; <sup>1</sup>Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina; <sup>2</sup>Edgewood 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 millifluidic chambers. A matrix of experiments was designed to isolate the SERS contributions arising from nano- and microscale porosity, long range 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 stripes of size from millimeters to centimeters. There is a range of important 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 dots. The new method is based on controlled drying of droplets from concentrated suspension on surfaces with intermediate hydrophobicity. We found that droplets of microsphere 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 Sayago<sup>2</sup>, Edgar Munoz<sup>1</sup>, Eva Terrado<sup>1</sup>, Manuel Alexandre<sup>2</sup>, M. Carmen Horrillo<sup>2</sup>, Jesus Lozano<sup>2</sup>, Jose Pedro Santos<sup>2</sup>, Esperanza Lafuente<sup>1</sup>, Wolfgang K. Maser<sup>1</sup>, Ana M. Benito<sup>1</sup>, Javier Gutierrez<sup>2</sup> and M. Teresa Martinez<sup>1</sup>; <sup>1</sup>Instituto de Carboquímica-CSIC, Zaragoza, Spain; <sup>2</sup>Laboratorio 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 and selectivity to hydrogen at room temperature in reversible and reproducible hydrogen detection processes.

## O6.16

**Synthesis of Noble Metal Nano-particles under Energetic Irradiation Fields.** Nobuhiro Maeda<sup>1</sup>, Taiji Hiroki<sup>1</sup>, Fuminobu Hori<sup>1</sup>, Shuichi Okuda<sup>1</sup>, Ryoichi Taniguchi<sup>1</sup>, Takao Kojima<sup>1</sup>, Tadashi Kambara<sup>2</sup>, Tomoko Abe<sup>2</sup> and Akihiro Iwase<sup>1</sup>; <sup>1</sup>Osaka Prefecture University, Sakai, Japan; <sup>2</sup>The Institute of Physical and Chemical Research(RIKEN), Saitama, Japan.

Dilute aqueous solutions with Au<sup>3+</sup> only, Pd<sup>2+</sup> only or Au<sup>3+</sup>+Pd<sup>2+</sup> ions and additives (PEG-MS;GPolyethylene Glycol Monostearate or SDS;GSodium Dodecylsulfate) are irradiated with 1 MeV  $\gamma$ -ray, 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, light 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 solutions and synthesizes Au nanoparticles. Size and shape of Au nanoparticles are examined by using a transmission electron microscope (TEM). The average diameter of the nanoparticles is 50 nm for 1 MeV  $\gamma$ -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  $\gamma$ -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.

## O6.17

**Macroporous CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> thin film sensors prepared by pulsed laser deposition on PMMA microsphere templates.** Ji-Doo Kim<sup>1,2</sup>, Avner Rothschild<sup>1</sup>, Takeo Hyodo<sup>1,3</sup> and Harry L. Tuller<sup>1</sup>; <sup>1</sup>Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Optoelectronic Materials Research Center, Korea Institute of Science and Technology, Seoul, South Korea; <sup>3</sup>Department 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 of various materials. It has been difficult, 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 presentation, we demonstrate successful application of the microsphere templating strategy to the fabrication of macroporous CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) films via pulsed laser deposition (PLD). Chemical and physical synthesis routes were combined to prepare macroporous CCTO thin films by pulsed laser deposition onto polymethylmethacrylate (PMMA) microsphere templated substrates, taking advantage of the unique virtues of the respective methods. Stable quasi-ordered hollow hemispheres with diameter and wall thickness of 800 nm and 100 nm, respectively, were obtained. Current-voltage and impedance spectroscopy measurements point to the crucial role played by grain boundary barriers in controlling the electrical properties of these films. The macroporous CCTO films have remarkably exceptional H<sub>2</sub> gas sensitivity compared with CCTO films deposited on untreated substrates. This demonstrates the virtues of combining thin film physical vapor deposition (PVD) techniques in concert with the microsphere templating method to produce 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 multilayer structures of compounds with complex chemistry. Moreover, the ability to control the macroporous structure of such films on different length scales from 50 nm to 5000 nm will enable 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.

## O6.18

**Synthesis of Novel ZnO Nanostructures: Spheres, Sheets, Needles, Tipped Nanorods and Wires, Polyhedral Cages, Shells and Microphone Like Structures.** Aurangzeb Khan<sup>1,2</sup> and Martin E. Kordesch<sup>1,2</sup>; <sup>1</sup>Physics and Astronomy, Ohio University, Athens, Ohio; <sup>2</sup>CMSS Program, Ohio University, Athens, Ohio.

Novel ZnO nanostructures such as nanowires, nanospheres, 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 nanospheres exhibit unique physical shapes and are hollow inside and their walls are composed of nanowires. Photoluminescence and cathodoluminescence at 300 K show typical emission spectra of ZnO. These structures can be studied for various applications in optoelectronics and sensors.

## O6.19

**Sequential Oxidation and Functionalization of Nanostructures: The Site-Specific Controlled Assembly of Different Nanoparticles on a Surface.** Daan Wouters<sup>1,2</sup> and Ulrich S. Schubert<sup>1,2</sup>; <sup>1</sup>Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands; <sup>2</sup>Dutch 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 for the use of a wide range of materials but also combines site-specificity with the possibility to sequentially construct architectures consisting of multiple components without affecting previously deposited structures. The technique used here is based on the local probe oxidation of octadecyl trichlorosilane monolayers. This technique converts the top methyl groups of the 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 photo electrochemical processes between semi conducting nanoparticles also in relation with the shape and size of the nanoparticles ensembles. As the first example we present the preparation of nanostructures consisting of arrays of gold nanoparticles with a diameters of 5 and 20 nanometer. 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 electrodeless deposition of gold or silver. before mentioned structures may be prepared by sequential local probe oxidation and surface modification routines. Existing structures on the surface will remain in tact during subsequent steps. If desired this method may be combined with dynamic plow lithography techniques. In addition we present the assembly of fluorescent ZnS/CeSe 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 fluorescence 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.

## O6.20

**Synthesis and applications of nanoparticles with photon upconverting properties.** Peng Zhang<sup>1</sup>, Khoi Nguyen<sup>1</sup>, Damon Wheeler<sup>1</sup>, Amanda Bernauer<sup>2</sup> and Snezna Rogelj<sup>2</sup>; <sup>1</sup>Chemistry, New Mexico Tech, Socorro, New Mexico; <sup>2</sup>Biology, New Mexico Tech, Socorro, New Mexico.

Phosphor particles have been used for decades in various applications. When ultraviolet light strikes the phosphor-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 phosphor 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 selection 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 ultrasensitive reporters, 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 100nm in diameter) with upconverting properties. It allows us to have more control over the size and distribution of the nanoparticles. This offers 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 spectra. We will 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, unaffected by common acids, bases, solvents, reducing agents, 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.

#### **O6.21**

##### **Supported TiO<sub>2</sub> Nanoparticles Prepared by Reactive-Layer-Assisted Deposition Studied by XPS, STM, STS and TPD.** Zhen Song<sup>1</sup>, Jan Hrbek<sup>2</sup> and Richard Osgood<sup>1</sup>;

<sup>1</sup>Applied Physics, Columbia University, New York, New York;

<sup>2</sup>Chemistry, Brookhaven National Laboratory, Upton, New York.

TiO<sub>2</sub> is an attractive and pervasive 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 TiO<sub>2</sub> nanoparticles were prepared by reactive-layer-assisted deposition (RLAD), in which Ti atoms are initially deposited on a multilayer of H<sub>2</sub>O (or NO<sub>2</sub>) grown on a Au(111) substrate at temperature <100 K. The chemical, structural and electronic properties of these oxide nanoparticles were then studied by XPS, STM, STS and TPD. Specifically, ~1 nm diameter TiO<sub>2</sub> particles, formed with an H<sub>2</sub>O reactive layer, were obtained after raising the substrate temperature to 300 K. The particles were found to preferentially aggregate around elbow sites of the reconstructed Au (111) surface, probably driven by the capillary force of liquid water drops that are pinned on the elbows. Use of NO<sub>2</sub> reactive layers yields TiO<sub>2</sub> nanoparticles (~1 nm at 300 K) with NO<sub>3</sub> radicals decorating their surfaces at temperatures below 500 K. The particles aggregate randomly distributed on the Au surfaces at temperatures below 500 K. The particle aggregates are randomly distributed on the Au surface. This could arise from the strong interaction of NO<sub>2</sub> with Au that the Au herringbone structure was lifted after adsorbing NO<sub>2</sub> on it. Further annealing was shown to induce desorption of N-containing species and to leave behind flat TiO<sub>2</sub> rutile and anatase particles (~5 nm after being annealed to 700 K) with various single or mixed facets. More extensive annealing at 700 K induced more rutile (100) facet particles. STS studies showed different electronic structure for different TiO<sub>2</sub> particle sizes. The band gap is ~3.8 eV for the ~5 nm TiO<sub>2</sub> particles, and it appeared larger for smaller particles. We are currently examining the chemical response of these nanoparticles. Thus far our TPD measurement has shown that the TiO<sub>2</sub>/Au system catalyzes the formation of formaldehyde from methanol. The nascent TiO<sub>2</sub> particles made from H<sub>2</sub>O reactive layer are also found to be able to reduce NO to NH<sub>3</sub>. This UHV compatible method for preparing well-defined TiO<sub>2</sub> nanoparticles is ideal for molecular-level studies of reaction mechanisms of photocatalytic processes on TiO<sub>2</sub> nanoparticle surfaces. This work is supported by DOE under the contracts of DE-FG02-90ER14104 and DE-AC02-98CH10886.

#### **O6.22**

##### **Sacrificial 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 isolable nanostructured metallic microshells. The metallic microshells retain all of the nanoscopic features that are inherent to the sacrificial 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.

#### **O6.23**

##### **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 can provide great utility due to their ability to directly manipulate and respond to their environments and will be used as future nanoactuators and nanosensors. Piezoelectric zinc oxide nanocrystals are grown by solution techniques on highly textured Ag (111) films. These nanocrystals have diameters ranging from 100 nm to 2 μm 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 perpendicular to the substrate. Since inversion symmetry is broken in this direction for wurtzite crystals, ZnO nanocrystals could grow in either the [0001] or [000 $\bar{1}$ ] direction. The piezoelectric coefficient ( $d_{33}$ ) 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 (000 $\bar{1}$ ) orientated rods that establish crystal growth directions from the substrates. In addition, using organic growth modifiers, e.g. citrate ions or diamine 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.

#### **O6.24**

##### **Simple Estimation of Nanoparticle Diameter Produced in a Flow Tube Reactor.** Kazunori Kuwana and Kozo Saito; Department of Mechanical Engineering, University of Kentucky, Lexington, Kentucky.

In many carbon nanotube synthesis methods, catalyst nanoparticles are formed via pyrolysis of a precursor such as ferrocene and iron pentacarbonyl. Since the diameter of a carbon nanotube is usually determined by the diameter of the catalyst nanoparticle, it is of great importance to control the size of nanoparticles. To do so, it is necessary to identify the key reaction parameters that influence nanoparticle size. To identify the key parameters, we recently applied a two-equation model, combined with computational fluid dynamics (CFD), to calculate the diameter of iron nanoparticles produced from ferrocene in a flow tube reactor. Our results indicated that Damköhler number was the most influential parameter; the calculated particle diameter agreed reasonably well with experimental data. For engineering purposes, simple analytical solutions offer a more convenient first estimation of particle diameter. They also clarify the dependence of nanoparticle diameter on each reaction parameter and enhance our understanding of the formation mechanism of nanoparticles. Thus we obtained two different analytical solutions for small and large Damköhler numbers and compared them with our earlier numerical simulations. We present the simplified one-dimensional model and its analytical solutions here. The model includes the effects of nucleation, collision, and diffusion of particles.

#### **O6.25**

##### **In-situ Study of Reduction and Re-oxidation of Mn<sub>3</sub>O<sub>4</sub> Nanoparticles.** Jenna Pike<sup>1</sup>, Siu-Wai Chan<sup>1</sup>, Feng Zhang<sup>1</sup> and Jonathan Hanson<sup>2</sup>; <sup>1</sup>Applied Physics and Applied Mathematics, Columbia University, New York, New York; <sup>2</sup>Chemistry, Brookhaven National Lab, Upton, New York.

Manganese oxides are widely used as catalysts and as components in Li-Mn batteries and solid oxide fuel cell cathodes. 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 Mn<sub>3</sub>O<sub>4</sub> nanoparticles with CO gas, and the re-oxidation of the resultant particles in pure oxygen. The in-situ experiments show that under a normal supply of CO, tetragonal Mn<sub>3</sub>O<sub>4</sub> reduces to cubic MnO, and the reduction temperature is controlled by Mn<sub>3</sub>O<sub>4</sub> nanoparticle size, as measured by XRD. As the initial Mn<sub>3</sub>O<sub>4</sub> particle size increases the temperature of MnO formation increases. The re-oxidation behavior of these particles is also dependent on the initial Mn<sub>3</sub>O<sub>4</sub> particle size. The formation of the unstable intermediate phase Mn<sub>5</sub>O<sub>8</sub> is observed in the oxidation of MnO ⇒ Mn<sub>3</sub>O<sub>4</sub> ⇒ Mn<sub>5</sub>O<sub>8</sub> ⇒ Mn<sub>2</sub>O<sub>3</sub> when the initial Mn<sub>3</sub>O<sub>4</sub> nanoparticles are 32 – 35 nm. Larger initial Mn<sub>3</sub>O<sub>4</sub> nanoparticles (45 nm) did not form Mn<sub>5</sub>O<sub>8</sub> during oxidation. Hausmannite (Mn<sub>3</sub>O<sub>4</sub>), the most stable of the manganese oxides, is prepared by mixing aqueous solutions of manganese nitrate and hexamethylenetetramine (HMT) at near room temperatures. Transmission electron microscope (TEM) results show that the size of the Mn<sub>3</sub>O<sub>4</sub> nanoparticles is controlled by varying reactant concentrations. An increase in either the HMT concentration or the manganese nitrate concentration results in a decrease in nanoparticle size. These results indicate the relationship between particle size and

reduction behavior may have significant consequences for the use of  $\text{Mn}_3\text{O}_4$  nanoparticles in reducing and oxidizing conditions.

#### **O6.26**

**Exploration of Iron Oxide Core-Shell Nanocomposites as Sensing and Catalytic Materials.** Lingyan Wang<sup>1</sup>, Jin Luo<sup>1</sup>, Xiajing Shi<sup>2</sup>, Susan Lu<sup>2</sup> and Chuan-Jian Zhong<sup>1</sup>; <sup>1</sup>Chemistry, State Univ. of New York at Binghamton, Binghamton, New York; <sup>2</sup>Systems Science and Industrial Engineering, State Univ. of New York at Binghamton, Binghamton, New York.

A key to the exploration of nanoparticles 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 (gold) 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 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 nanoparticles with controllable surface properties for molecularly-mediated assembly of the nanoparticles. By controlling the reaction temperatures and manipulating the capping agent properties and solution compositions, the size, shape, composition, and monodispersity can be tailored. The nanoparticles and thin film assembly are characterized by an array of techniques, including TEM, ED, DCP, XPS, XRD, FTIR, SQUID and Electrochemistry techniques. The molecularly-mediated nanoparticle assemblies of the core-shell nanostructures are exploited as sensory materials for detecting toxic gases and volatile organic compounds. The results have also provided important insights into the design of core-shell nanocomposites as catalysts for catalytic applications.

#### **O6.27**

**Structural evolution of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$  thin films for SOFCs and catalysis.** Nina Orlovskaya<sup>1</sup>, Anthony Coratolo<sup>1</sup>, Christopher Johnson<sup>2</sup> and Randall Gemmen<sup>2</sup>; <sup>1</sup>Drexel University, Philadelphia, Pennsylvania; <sup>2</sup>National Energy Technology Laboratory, Morgantown, West Virginia.

Nanostructured  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$  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 ( $\text{CO} + \text{H}_2$ ) production by direct conversion of methane and other basic hydrocarbon gases. The structure of  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3$  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  $\text{La-Sr-Cr-Co-O}$  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 Mn, Al, Si, Ni, Ti, S, have been used for the film deposition. The substrates were heated up to 600°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 transform 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  $\text{LaCrO}_4$  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 ( $\text{H}_2/\text{N}_2$ ). 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 nanoporosity, which was almost absent in case of the 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 impurities in the substrate materials, especially Si and Al that form non-conductive oxides upon oxidation. The lowest ASR equals to 0.005  $\text{ohm}\cdot\text{cm}$  is reported for the CROFER APU 22 alloy that has the lowest level of impurities (Si = 0.01wt%, Al=0.01wt%) and has been coated with  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$  thin film. The research results are important for design of lower temperature SOFCs as well as perovskite catalytic membrane reactors.

#### **O6.28**

**A Non-Catalytic Silicon Nanowire Fabrication Approach and Its Device-Use Assessment.** Yuan Hao, Ali Kaan Kalkan and Stephen J. Fonash; CNEU, 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.

#### **O6.29**

**Changes in Oligonucleotide Conformation on Nanoparticle Surfaces by Modification with Mercaptohexanol.** Sunho Park<sup>1</sup>, Katherine Alice Brown<sup>2</sup> and Kimberly Hamad-Schifferli<sup>1,2</sup>; <sup>1</sup>Department of Mechanical Engineering, M.I.T., Cambridge, Massachusetts; <sup>2</sup>Biological 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 unobstructed 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 thus inhibit hybridization by preventing base pairing. We use chemical modification of the nanoparticle surface with 6-mercapto-1-hexanol (MCH) to control oligo conformation oligo so that the DNA can achieve a conformation that facilitates hybridization. The Ferguson plot method is used to evaluate the change in effective size of 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.

#### **O6.30**

**Nanotubes as Stationary Phase in Microfabricated Gas Concentrators and Separators.** Michael Stadermann<sup>1</sup>, Brian Dick<sup>1</sup>, Christopher Bailey<sup>1</sup>, Ulrich Bonne<sup>2</sup>, Robert Higashi<sup>2</sup>, Alex Noy<sup>1</sup> and Olga Bakajin<sup>1</sup>; <sup>1</sup>Chemistry & Materials Science, Lawrence Livermore National Laboratory, Livermore, California; <sup>2</sup>Honeywell Laboratories, Plymouth, Minnesota.

Separation and characterization of substances has been restricted to laboratory operations in the past, and 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. In 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.

#### **O6.31**

**Catalytic activity of nanosize amorphous iron in the process of conversion of cyclohexane.** Minasyan Varja<sup>2</sup>, Grigoryan Susanna<sup>1</sup> and Razmik Malkhasyan<sup>1</sup>; <sup>1</sup>Chemical Physics Institute of NAN, Yerevan, Armenia; <sup>2</sup>Scientific production enterprise "ATOM", Yerevan, Armenia.

Nanostructured materials have wide use in catalytic processes for the

last years. These materials are obtained by different physical and chemical methods. In this paper it is presented the nanosize amorphous iron Fe obtained by means of non-equilibrium quantum-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 Al<sub>2</sub>O<sub>3</sub> (with Surface specific = 60m<sup>2</sup>/gr, radius of pore is 370Å and size of particle is 2 nm), preliminary heated to 400 oC. The catalytic activity of amorphous Fe and crystalline Fe is compared in the reaction of dehydrogenation and hydrogenolysis of cyclohexane (H<sub>2</sub> is gas-carrier, under atmospheric pressure, and T = 250-400 oC). 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 commercially important Fischer-Tropsch synthesis reaction (hydrogenation of CO) within low temperature range 200-350 oC.

### O6.32

**Aerogel-Nanotube Composites: Growth of Carbon Nanotubes on Catalytically-Active Aerogel Monoliths using Chemical Vapor Deposition.** Stephen A. Steiner<sup>1</sup>, Mildred S. Dresselhaus<sup>1</sup>, Jing Kong<sup>1</sup>, Theodore F. Baumann<sup>2</sup> and Joe H. Satcher<sup>2</sup>; <sup>1</sup>Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Chemistry 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. The unusually high surface areas (250 to 1,000 m<sup>2</sup>/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, aerogels with carbon nanotubes integrated into their structure 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 epoxide-assisted gelation 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 950°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.** Yuan Sun<sup>1</sup>, Rebecca Isseroff<sup>2</sup>, Cheryl Shonbrun<sup>2</sup>, Michelle Forman<sup>2</sup>, Anatoly I. Frenkel<sup>3</sup>, Kwanwoo Shin<sup>4</sup>, Tadanori Koga<sup>1</sup>, Henry White<sup>1</sup>, Miriam H. Rafailovich<sup>1</sup> and Jonathan C. Sokolov<sup>1</sup>; <sup>1</sup>Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, New York; <sup>2</sup>Stella K Abraham High School, Hewlett, New York; <sup>3</sup>Physics, Yeshiva University, New York, New York; <sup>4</sup>Materials Science and Engineering, K-JIST, Oryong-dong, Kwang-ju, 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 4.6 nm and 2.0 nm for the 1- and 2-phase particles, respectively. Electron diffraction confirmed that their structure was FCC. The lattice constant *a*<sub>0</sub>, was 3.71 angstrom and 3.77 angstrom for the 1- and 2-phase particles, respectively, which were slighter shorter than 3.89 angstrom of the Pd bulk value. The particles were also analyzed 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 by the NSF-MRSEC program. AIF acknowledges support by the U.S. Department of Energy, Grant No. DE-FG02-03ER15477.

### O6.34

**Nanocrystalline Diamond as an Interface for Biomedical Applications.** Zhenqing Xu<sup>1,2</sup> and Ashok Kumar<sup>1,2</sup>; <sup>1</sup>Mechanical Engineering, University of South Florida, Tampa, Florida; <sup>2</sup>Nanomanufacturing 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 idea interface that is compatible with microelectronics process 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 deposit continuous film at nanometer range, easier coating of substrates with irregular geometries and the unique electrochemical behavior result from NCD film/s 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 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 voltammograms (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 Graphen.** Kazuyuki Okazaki-Maeda<sup>1</sup>, Yoshitada Morikawa<sup>2,1</sup>, Shingo Tanaka<sup>3</sup> and Masanori Kohyama<sup>3,1</sup>; <sup>1</sup>CREST, Japan Science and Technology Agency, Kawaguchi, Japan; <sup>2</sup>Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Japan; <sup>3</sup>Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ikeda, Japan.

Platinum (Pt) particles supported on carbon materials are used as electrode catalyst of fuel cell. We have to examine atomic structure and electronic state in detail to know the characteristic properties. Therefore we examined atomic structure and electronic state of Pt cluster supported on graphen, using the first-principles calculations based on the density functional theory (DFT). We constructed the 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<sub>10</sub> cluster as the calculating surface unit cell. We used the periodic slab model separated by vacuum region of about 25Å. At first, we examined the interaction between graphen and Pt(111) monolayer. The distance between graphen and Pt(111) is 3.48Å and the adhesive energy is 0.09 eV/atom. The density of states (DOS) for Pt(111)/graphen system is the same with the sum of DOS's for graphen and Pt(111) monolayer. These results show that the interaction between graphen and Pt(111) monolayer is very weak. When Pt is adsorbed on TiO<sub>2</sub>(110), the Pt adatom strongly interacted with the vacancy at surface. Some defect in graphen may do an important role even in the case of Pt on graphen. Next, we examined the interaction between graphen and the Pt cluster consisting of ten atoms. The shape of Pt<sub>10</sub> cluster is a hexagonal bottom layer with seven atoms and a triangular top layer with three atoms. The distance between graphen and the bottom layer is about 2.7Å. This distance is shorter than that of the adhesion of Pt(111) monolayer. Therefore, it can be said that the interaction between the Pt<sub>10</sub> cluster and graphen is stronger than that between the Pt(111) monolayer and graphen. Moreover, the center atom in the hexagonal bottom layer is nearer to graphen than other atoms and that distance is about 2.5Å. If there is a defect on graphen, 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 on graphen in detail on the day. This research was supported by the CREST, JST.

#### **O6.36**

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

Encapsulation of metallic nanoparticles in electrospun polymer nanofibers provides a perfect solution to their durable usages in solid state sensors and catalysis. The *in situ* synthesis of gold and 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) (P4VPy-*b*-PMMA), 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 embedment location. Thermal/oxidative stability and other physical properties of metallic nanoparticles encapsulated in nanofiber matrices were characterized and discussed.

#### **O6.37**

**Analytical TEM Observation of Gold Nano-Particles on Cerium Oxide.** Tomoki Akita<sup>1</sup>, Koji Tanaka<sup>1</sup>, Masanori Kohyama<sup>1</sup> and Masatake Haruta<sup>2</sup>; <sup>1</sup>Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan; <sup>2</sup>Materials Chemistry Course, Tokyo Metropolitan University, Hachioji, Tokyo, Japan.

It was reported that Au/CeO<sub>2</sub> 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 CeO<sub>2</sub> surface were responsible for low temperature water gas shift reaction. However, the detailed structure of Au particles on CeO<sub>2</sub> was not investigated directly. Because it is difficult to observe small Au clusters on CeO<sub>2</sub> by conventional transmission electron microscopy (TEM) due to the disturbance of the diffraction and phase contrast by the CeO<sub>2</sub> substrate. The structure of Au/CeO<sub>2</sub> 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 CeO<sub>2</sub> support. However, the CeO<sub>2</sub> 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 CeO<sub>2</sub>. In this work, TEM observations were performed on a model catalyst sample that was prepared using a CeO<sub>2</sub> support with a lower surface area and poly crystalline substrate in order to study the interface structure between metal particles and CeO<sub>2</sub>. Gold nanoparticles were deposited on commercially-produced, high-purity CeO<sub>2</sub> powder using the deposition precipitation method, which is utilized for the preparation of highly dispersed Au particles on metal oxide. The Au/CeO<sub>2</sub> model samples were also prepared by the vacuum deposition on poly crystalline CeO<sub>2</sub> substrate. A JEOL 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 CeO<sub>2</sub> support with a preferred orientation relationship. The Au{111} plane was parallel to the CeO<sub>2</sub>{111} plane and the <110> direction of Au and CeO<sub>2</sub> 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 CeO<sub>2</sub> 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 at the contact interface are strongly connected to the CeO<sub>2</sub> surface. It was also observed that the Au particles were dispersed as smaller particles again after irradiation by electron beam.

#### **O6.38**

**Colloidal-Au Replacement Assay Based on Surface Plasmon Resonance and PEGylated Gold Nanoparticles.** Seiji Takae<sup>1</sup>, Yoshitsugu Akiyama<sup>1</sup>, Yuichi Yamasaki<sup>1</sup>, Yukio Nagasaki<sup>2</sup> and Kazunori Kataoka<sup>1,3</sup>; <sup>1</sup>Materials Science and Engineering, The University of Tokyo, Tokyo, Japan; <sup>2</sup>Tsukuba Research Center for Interdisciplinary Materials Science, Tsukuba University, Tsukuba, Japan; <sup>3</sup>Center 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-poly(ethylene glycol) (PEG) disulfide dimer revealed a remarkably larger shift in plasmon angle through the binding onto Ricinus communis agglutinin (RCA120)-immobilized 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 plasmon 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 substituted 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.

#### **O6.39**

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

Highly oriented ZnO, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> 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. Their pH sensing properties have been investigated in this paper. The sensitivities of the ZnO, anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> nanorods are 44.8, 23.4, 55.5 and 57.6 mV/pH, respectively, in the range of pH3 to pH11. The enhancement of the pH sensing properties of the TiO<sub>2</sub> 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.

#### **O6.40**

**Nanowire for Detection of Biological Species.** Kyung Ah Jeon<sup>1</sup>, Jong Hoon Kim<sup>1</sup>, K. H. Yoo<sup>2</sup>, Hyo Il Jung<sup>3</sup> and Sang Yeol Lee<sup>1</sup>; <sup>1</sup>Electrical and Electronic Engineering, Yonsei University, Seoul, South Korea; <sup>2</sup>Department of Physics, Yonsei University, Seoul, South Korea; <sup>3</sup>School 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. We report chemical sensitivity of silicon nanowire. PNA modified Si NWs 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 exploited in vivo diagnostics.

#### **O6.41**

**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 dependant resistivity, is an attractive ternary system for negative temperature coefficient (NTC) thermistor applications. Structural and electrical characteristics are presented for thick film Mn<sub>1.56</sub>Co<sub>0.96</sub>Ni<sub>0.48</sub>O<sub>4</sub> thermistor produced by thermal spraying. The composition of Mn-Co-Ni-O spinel, owing to its large temperature dependant resistivity, is an attractive ternary system for negative temperature coefficient (NTC) thermistor applications. Structural and electrical characteristics are presented for thick film Mn<sub>1.56</sub>Co<sub>0.96</sub>Ni<sub>0.48</sub>O<sub>4</sub> thermistor produced by thermal spraying. The composition of Mn<sub>1.56</sub>Co<sub>0.96</sub> Ni<sub>0.48</sub>O<sub>4</sub> 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 nanostructured 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 °C/3h. The electrical resistivity of the coatings was made using four-point-probe method in the temperature range of 20 °C to 210 °C. 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 °C/3h varies from 4121 ohm-cm (33 °C) to 65 ohm-cm (207 °C) with an activation energy of 0.278 eV. For the coating heat treated at 700 °C/3h, the resistivity varies from 7887 ohm-cm (33 °C) to 121 ohm-cm (207 °C) and has an activation energy of 0.287 eV. To estimate the thermistor constant B, the resistance values were expressed as  $R(T)=R_0 \cdot \exp(B/T)$ , where  $R_0$  is the resistance when the temperature T approaches infinity. The estimated B for samples heat treated at 600 °C/3h and 700 °C/3h were 3225K and 3333K, respectively. The as-sprayed sample, which has the rock salt structure, shows a slightly complex temperature-dependence resistivity which begins to decrease on heating above 50 °C probably due to the change in valence state of cobalt. The TCR, the temperature coefficient of resistivity, for 600 °C/3h heat treated sample is equal to -1~-4%, in the temperature range from 20 °C to 200 °C, which is in good agreement with reported values [1]. Reference: [1] Hideo Arima, in Thick-Film Sensors, M. Prudenziati, ed. Elsevier Sciences B.V. 1994, p 127 Acknowledgement: This work is supported by the MRSEC program of NSF. Award #DMR-0080021.

SESSION O7: Biosensors II  
Chairs: Nicholas Kotov and Chuan-Jian Zhong  
Wednesday Morning, November 30, 2005  
Room 200 (Hynes)

#### 8:15 AM O7.1

##### AuFe alloy nanoparticles for biological applications.

Katherine Alice Brown<sup>1</sup> and Kimberly Hamad-Schifferli<sup>2,1</sup>;

<sup>1</sup>Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; <sup>2</sup>Mechanical 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 Fe<sup>3+</sup> and Au<sup>3+</sup> in water to yield alloy nanoparticles. Bulk studies of AuFe alloys have shown interesting magnetic and crystallographic properties, but previously nanoparticle synthesis techniques have been limited to electron beam methods, resulting in particles of limited solubility. Solution phase synthesis allows far more versatile particles. The elemental content of Fe varies from 1%-3% and can be increased by decreasing the relative amounts 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 \*O7.2

**Strategies for the Design and Readout of Ultrahigh Density Immunodiagnostic Platforms.** Marc Porter, Hye-Young Park, Jeremy Driskell, Karen Kwarta, Betsy Yakes, Jill Uhlenkamp, Rachel Millen, Nikola Pekas, John Nordling and Robert Lipert; Chemistry, Iowa State University, Ames, Iowa.

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 spectroscopic, 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, ultralow 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 O7.3

##### Carbon nanotube biosensors with DNA aptamers as molecular recognition elements.

Jeong-O Lee<sup>1</sup>, Hye-Mi So<sup>1</sup>, Keehoon Won<sup>1</sup>, Yong Hwan Kim<sup>1</sup>, Beyong Hwan Ryu<sup>1</sup>, Pil Sun Na<sup>2,1</sup> and Byung-kye Kim<sup>3,1</sup>; <sup>1</sup>Advanced materials Div., Korea Research Institute of Chemical Technology, Daejeon, South Korea; <sup>2</sup>Department materials engineering, Chungnam National Univ., Daejeon, South Korea; <sup>3</sup>Department 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 CDI-Tween linking 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-FET, sudden drop of conductance has observed, thereby demonstrating the possibility realizing highly selective nanotube-based biosensors.

#### 9:15 AM O7.4

##### Large-scale, label-free, parallel electrical detection of proteins, nucleic acids and viruses by high-throughput ultrasensitive nanowire FET arrays.

Gengfeng Zheng<sup>1</sup>, Fernando Patolsky<sup>1</sup> and Charles M. Lieber<sup>1,2</sup>; <sup>1</sup>Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; <sup>2</sup>Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

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. Tens 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 O7.5

##### Complementary Detection of Prostate-Specific Antigen Using Indium Oxide Nanowires and Carbon Nanotubes.

Marco Curireli<sup>1</sup>, Chao Li<sup>3</sup>, Henry Lin<sup>4</sup>, Mark E. Thompson<sup>1,2</sup>, Fumiaki Ishikawa<sup>2</sup>, Ram Datar<sup>4</sup>, Richard Cote<sup>4</sup> and Chongwu Zhou<sup>3,1</sup>; <sup>1</sup>Chemistry, University of Southern California, Los Angeles, California; <sup>2</sup>Material Science, University of Southern California, Los Angeles, California; <sup>3</sup>Electrical Engineering/Electro-physics, University of Southern California, Los Angeles, California; <sup>4</sup>Pathology, 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 onsite 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: 0.14nM) while the conductivity went down of 2% when nanotubes devices were used (PSA level: 1.4nM). 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 O7.6

##### Synthesis and Characterization of Novel Glucose-Sensitive

**Nanogels.** Shuiqin Zhou and Yongjun Zhang; Department of Chemistry and The Center for Engineering Polymer Materials of the College of Staten Island, The City University of New York, Staten Island, New York.

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 can 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 candidate 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 \*O7.7

**Plasmonic Nanostructures for SERS sensing: comparing geometries and local field properties.** Naomi J. Halas<sup>7,1,3</sup>, Chris Oubre<sup>2,7</sup>, Peter Nordlander<sup>2,1,7</sup>, Hui Wang<sup>3,7</sup>, Joseph Jackson<sup>2,7</sup>, Nate Grady<sup>2,7</sup>, Felicia Tam<sup>2,7</sup>, Thomas Huser<sup>1,4,5,6</sup>, Chad Talley<sup>4,6</sup>, Chris Hollars<sup>4,6</sup>, Stephen Lane<sup>5,6</sup>, Carly Levin<sup>3,7</sup> and Muhammed Gheith<sup>1,3,7</sup>; <sup>1</sup>Department of Electrical and Computer Engineering, Rice University, Houston, Texas; <sup>2</sup>Department of Physics and Astronomy, Rice University, Houston, Texas; <sup>3</sup>Department of Chemistry, Rice University, Houston, Texas; <sup>4</sup>Chemical and Materials Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, California; <sup>5</sup>Physics and Advanced Technologies Directorate, Lawrence Livermore National Laboratory, Livermore, California; <sup>6</sup>NSF Center for Biophotonics Science and Technology, University of California, Davis, Sacramento, California; <sup>7</sup>Laboratory for Nanophotonics, Rice University, Houston, Texas.

Our ability to design and fabricate high sensitivity nanosensors based on local electromagnetic field driven processes such as surface 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. In this study we perform a comparison of experimental 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 structures. In addition, the effect of local nanoscale roughness was addressed both experimentally and theoretically.

#### 11:00 AM O7.8

**Urease-composite Nanofibers as Urea Biosensing Material.** Katarzyna Magdalena Sawicka and Perena Gouma; 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 ((NH<sub>2</sub>)<sub>2</sub>CO). More than 90% of urea is excreted through the kidneys, and the rest gets emitted through the gastrointestinal 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 urea biosensors currently available utilize urease (urea aminohydrolase) 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. urease  $H_2N-CO-NH_2+H_2O \longrightarrow NH_3+H_2N-CO-OH \longrightarrow H_2N-CO-OH+H_2O \longrightarrow NH_3+H_2CO_3 \longrightarrow 2NH_4^+ +2HCO_3^- + H^+ + OH^-$  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 phosphate buffered saline and polyvinylpyrrolidone (PVP) were prepared by the electrospinning technique. Reactivity measurements for urease/polymer nanocomposite fiber mats 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-composite nanofibers was done with Scanning, and Transmission 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 O7.9

**Functionalization of Vertically Aligned Carbon Nanofiber Electrodes for Biological Detection.** Sarah Elyse Baker, Kiu-Yuen Tse, Tami Lasseter Clare, Chang-Soo Lee, Eve Hindin and Robert J. Hamers; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

Vertically aligned carbon nanofibers are a unique class of carbon-based materials that have promising properties as electrodes 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 glass). Additionally, the nanoscale diameter 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 either 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 forest 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  $2.3 \times 10^{14}$  molecules per cm<sup>2</sup>. 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 sensor may have greater sensitivity. This chemistry was 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 O7.10

**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 Lu 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 ambient conditions has been one of the hallmarks in biology. Employing such a process in nanoscale science and engineering can result in novel nanomaterials that rival or even exceed the structural and functional properties of naturally occurring materials. Toward this goal, we have taken advantage of recent advance 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 analyte 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 such as metal ions [3] or organic molecules [4] have been demonstrated. Because of the highly intense color change from the blue assembled gold nanoparticles to the disassembled 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 resulted in a new derivative of DNazyme that allows a tunable assembly of nanoparticle and thus tunable dynamic range of detection [3]. In addition, a detailed understanding of DNazyme and nanoparticle interactions resulted in substantial shortening of detection time from about 2 hours to less than five minutes, and from 50  $\mu$ C heating to ambient temperature operation [8]. In addition to controlled assembly of materials in responsive to chemical stimuli, biology also controls the disassembly of materials in responsive to chemical stimuli so that useful materials can be released or harmful processes can be prevented. We have recently succeeded in employing such a process in disassemble gold nanoparticle aggregates in responsive to metal ions such as Pb<sup>2+</sup>. This endeavor has resulted in even further improvement of the colorimetric sensor by transforming a light-down sensor into a light-up sensor. Light-up sensor is preferred

for practical applications since human eyes and most equipment are more sensitive to light-up sensors than to light-down sensors. Recent progress in this work will be presented. 1. Yi Lu, Chem. Euro. J. 8, 4588-4596 (2002). 2. Peter J. Brueshoff, Jing Li, Anthony J. Augustine III, and Yi Lu, *Combinator. Chem. High Throughput Screening* 5, 327-335 (2002). 3. Juewen Liu and Yi Lu, *J. Am. Chem. Soc.* 125, 6642-6643 (2003). 4. Juewen Liu and Yi Lu, *Anal. Chem.* 76, 1627-32 (2004). 5. Juewen Liu and Yi Lu, *J. Fluoresc.* 14, 343-354 (2004). 6. Juewen Liu and Yi Lu, *Chem. Mater.* 16, 3231-3238 (2004). 7. Andrea K. Brown, Caroline M.-B. Pavot, Jing Li, and Yi Lu, *Biochemistry* 42, 7152-7161 (2003). 8. Juewen Liu and Yi Lu, *J. Am. Chem. Soc.* 126, 12298-12305 (2004).

#### 11:45 AM O7.11

##### Understanding Surface Biosensor Liquid Crystal Textures.

Benjamin Wincure and Alejandro D. 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 nano- and mesoscopic regions. Despite their importance to 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 a tensor 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 opposing front easy axes act as a mechanism to create defects and director 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. Kotov<sup>1</sup>, Jaebom Lee<sup>1</sup> and Alexander Govorov<sup>2</sup>;

<sup>1</sup>Chemical Engineering, University of Michigan, Ann Arbor, Michigan;

<sup>2</sup>Physics, 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 concentrations and other parameters for intricate geometries 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 designing 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. Plasmon-exciton interactions result in tremendous enhancement of luminescence and for some systems in characteristic wavelength shift depending on the analyte concentration. Understanding plasmon-exciton interactions will contribute to the photonics and nanoscale optics and create a knowledge base for other technologies such as lasing in nanomaterials, energy conversion, and nanoscale electronics.

#### 1:45 PM \*O8.2

##### 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 O8.3

##### Surface Enhanced Raman Scattering on Physically

Self-assembled Ag Nanorod Arrays. Motofumi Suzuki<sup>1</sup>, Yoshinori

Wada<sup>1</sup>, Kaoru Nakajima<sup>1</sup>, Kenji Kimura<sup>1</sup>, Takao Fukuoka<sup>2</sup> and

Yasushige Mori<sup>3</sup>; <sup>1</sup>Department of Micro Engineering, Kyoto

University, Kyoto, Kyoto, Japan; <sup>2</sup>Kyoto CREATE, JST, Seika,

Kyoto, Japan; <sup>3</sup>Department 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-parallel major axis on a template layer of SiO<sub>2</sub> having a strongly anisotropic surface morphology. [1] In this work, we report the surface enhanced Raman scattering (SERS) on these Ag nanorod arrays. Template layers of SiO<sub>2</sub> with anisotropic surface morphology were prepared by the serial bideposition technique on a glass substrate in our dynamic oblique deposition (DOD) apparatus. During the serial 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 serial 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 self-shadowing, the major axes of the Ag nanorods are aligned perpendicular to the deposition plane of SiO<sub>2</sub>. 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 of 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) L193.

#### 3:30 PM O8.4

##### Electrosynthesis of Magnetostrictive Nanosensor Array.

Suigong Li, Lisa Orton 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-boron 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 \*O8.5

##### Single-Walled Carbon Nanotube Networks for Sensor

Applications. Elena Bekyarova, Mikhail E. Itkis 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 are an attractive electronic device 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

discuss a number of derivatives, including: SWNTs with covalently attached poly(m-aminobenzene sulfonic acid), SWNT-PABS, and SWNTs with covalently attached octadecylamine, SWNT-ODA. We will also address the effect of film thickness on the electronic properties of the SWNT networks and sensor performance.

#### 4:15 PM O8.6

**Nanoparticle SnO<sub>2</sub> films as gas sensitive membranes.** Benedikt Schumacher<sup>1,2</sup>, Dorothee Vinga Szabo<sup>2</sup>, Sabine Schlabach<sup>2</sup>, Rolf Ochs<sup>2</sup>, Harald Mueller<sup>3</sup> and Michael Bruns<sup>3</sup>; <sup>1</sup>Institute for Microsystem Technology (IMTEK), Albert-Ludwigs-University, Freiburg, Germany; <sup>2</sup>Institute for Materials Research III (IMF III), Forschungszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany; <sup>3</sup>Institute 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 Nose the central gas-sensitive microarray is based on a sputtered SnO<sub>2</sub> layer. Its 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 4x8mm<sup>2</sup>. 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. SnO<sub>2</sub>/SiO<sub>2</sub> 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 sensor 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 SnO<sub>2</sub> 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, SnCl<sub>4</sub> was selected; Ar with 20vol% O<sub>2</sub> was used as reaction gas. Particles crystallized in the tetragonal cassiterite structure. It was found that a feeding rate of 0.1ml/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. In a second step, SiO<sub>2</sub>-coated SnO<sub>2</sub> nanoparticles and nanoporous gas sensitive layers were produced. The SiO<sub>2</sub> coating had a thickness of 0.3 to 0.5nm and showed amorphous like structure. Also in this case residual chlorine disappeared by heating the layer at 575K. It is expected that the coating is gas permeable and does not affect sensitivity. Gas sensitivity tests are on the way.

#### 4:30 PM O8.7

**Mediator-Template Assembly of Metal Nanoparticles and Sensing Applications.** I-Im Stephanie Lim, Mathew M. Maye, Jin Luo and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

A key to the design and control of nanoparticle-derived functional nanostructures such as sensory nanomaterials is the understanding of kinetic and thermodynamic factors that govern the assembly of the nanoparticles. Such understanding is however hampered by the lack of direct experimental measurements of the assembly process. This paper describes a study of the kinetic and thermodynamic properties for the mediator-template assembly of gold nanoparticles in solution based on spectrophotometric 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 route in which a thioether-based multidentate ligand (e.g., (MeSi(CH<sub>2</sub>SMe)<sub>3</sub>) functions as a mediator whereas the tetraoctylammonium shell molecules function as template agents. The temperature dependence of the SP band in the mediator-template assembly process is determined, from which 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 O8.8

**DNA-Functionalized Carbon Nanotubes for Chemical Sensing.** Cristian Stai<sup>1</sup>, Michelle Chen<sup>2</sup>, Alan Gelperin<sup>3,4</sup> and Alan T. Johnson<sup>1</sup>; <sup>1</sup>Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>2</sup>Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>3</sup>Department of Neuroscience, University of Pennsylvania, Philadelphia, Pennsylvania; <sup>4</sup>Monell Chemical Senses Center, Philadelphia, Pennsylvania.

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 gaseous 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 analytes 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 rapid, stable, and long-lasting sensing capability. Our results 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 O9: Poster Session: Nanoparticles and Nanostructures in Sensors and Catalysis III  
Chairs: Wayne Daniell, Chuan-Jian Zhong and Shuiqin Zhou  
Wednesday Evening, November 30, 2005  
8:00 PM  
Exhibition Hall D (Hynes)

#### O9.1

**Functionalized Y-junction singlewall carbon nanotube mats for carbon monoxide sensing applications.** Harindra Vedala, Somenath Roy, Jun Huang and Wonbong 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. Among 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 K<sub>2</sub>PtCl<sub>6</sub> and SnCl<sub>4</sub>.5H<sub>2</sub>O. Carbon monoxide is detected from the change 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.

#### O9.2

**Selective Detection of Cholesterol Using Carbon Nanotube Based Biochip.** Somenath Roy, Harindra Vedala, Jun Huang and Wonbong Choi; Mechanical and Materials Engineering, Florida International University, Miami, Florida.

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 cholesterol oxidase (*Pseudomonas fluorescens*) on the electrode is done by entrapment of the enzyme in a bio-friendly, water insoluble polymer, polyvinyl alcohol (PVA), which also increases the hydrophilicity of the carbon nanotube (CNT) surface (with experimental evidence) and thereby facilitating the intimate attachment of the protein molecules. For superior heterogenous 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 voltammograms exhibit efficient detection of cholesterol in the range of 100-300 mg/dl, which covers the entire range of possible cholesterol concentration in human blood. Horseradish peroxidase (HRP) is coimmobilized on the working electrode and the influence of relative concentrations of the enzymes 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 interferents, like glucose, ascorbic acid and uric acid, present in the physiological fluids, is also examined. 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 Nano-dot Array.** Jun-ichi Fujita<sup>1,4</sup>, Takahito Mukawa<sup>1,4</sup>, Satoshi Okada<sup>1,4</sup>, Ryota Kobayashi<sup>1,4</sup>, Masahiko Ishida<sup>2,4</sup>, Toshinari Ichihashi<sup>2,4</sup>, Yukinori Ochiai<sup>2,4</sup> and Shinji Matsui<sup>3,4</sup>; <sup>1</sup>Institute of Applied Physics, University of Tsukuba, Tsukuba, Japan; <sup>2</sup>NEC Fundamental Res. Labs., Tsukuba, Japan; <sup>3</sup>LASTII, University of Hyogo, Hyogo, Japan; <sup>4</sup>CREST-JST, Kawasaki, Japan.

We report a successful demonstration of a position control technique for carbon nanotube (CNT) growth catalyzed by an iron nano-dot array, which was fabricated by using electron beam induced chemical vapor deposition (EB-CVD). The point irradiation of an electron beam with a ferrocene source gas produced an amorphous 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 segregation of iron nano-particles[1], whose size was almost proportional 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 nanoparticles on a Si substrate with thermal 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 carried out at 800°C under 40 mmHg of ethanol vapor induced 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 still 5 to 10%. The growth yield seemed dependent on the surface condition of the SiO<sub>2</sub>, 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.*, 43 (2004) 3799. [2] T. Ichihashi, J. Fujita, M. Ishida, and Y. Ochiai, *Phys. Rev. Lett.*, 92 (2004) 215702-1.

**O9.4**  
**Nitrogen and Fluorine roles in Visible-Light-Driven Anion-Doped TiO<sub>2</sub> Photocatalysis.** Li Di, Naoki Ohashi, Shunichi Hishita, Taras Kolodiaznyi and Hajime Haneda; Advanced Materials Lab, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Many attempts have been made recently in the direction of anion-doped TiO<sub>2</sub> 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 TiO<sub>2</sub> powders (NTO, FTO, NFTO) were synthesized by spray pyrolysis (SP) from a mixed aqueous solution of TiCl<sub>4</sub> and one of the N-precursor (H<sub>2</sub>NCONH<sub>2</sub>), F-precursor (HF) and N-F-co-precursor (NH<sub>4</sub>F). 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, NH<sub>3</sub>-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

TiO<sub>2</sub> resulted in not only the improvement in visible-light absorption but also the creation of surface oxygen vacancies. F-doping produced several beneficial effects including the creation of surface oxygen vacancies, the enhancement of surface acidity and the increase of Ti<sup>3+</sup> ions. Doped N atoms formed a localized energy state above the valence band of TiO<sub>2</sub>, whereas doped F atoms themselves had no influence on the band structure. The photocatalytic tests indicated that the NFTO demonstrated the highest visible-light activity for decompositions of both acetaldehyde 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 Vis photocatalysts with high performances.

**O9.5**  
**Studies on Nanoferroelectric Ceramic Based on Nd Doped PZT.** R. N. P. Choudhary, S. K. S. Parrashar, Awalendra 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 novel behavior when their crystallite size falls below a 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 effects depending on the extent of reduction in size. The present work aims to investigate crystallite size effect on the dielectric, ferroelectric and electrical conduction behavior of Nd substituted PZT based nanocrystalline ceramic oxide, Pb<sub>0.92</sub>Nd<sub>0.08</sub>(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)<sub>0.98</sub>O<sub>3</sub> abbreviated as PNZT. 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 strain contribution, 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 milled powder (green powder) has been noticed on sintering the pellet of milled 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 milled and 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 Ultrahigh Crystalline Titania Nanotubules.** O-Bong Yang, Mahmood Alam Khan and Hyunul 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 conduction paths for the photo-excited electrons through the tube channel. TiO<sub>2</sub> nanotubes with low crystallinity as compared with high crystalline TiO<sub>2</sub> nanoparticles have limitations regarding their application as advanced materials in photo-induced reactions. However, very fewer efforts 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 TiO<sub>2</sub> nanotube as high as high crystalline TiO<sub>2</sub> nanoparticles. Detailed structural and photocatalytic properties of the titania nanotubes were elucidated. We prepared high surface area Titania nanotube, which was only anatase phase, by hydrothermal method and we chemically modify 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, TEMEDX 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. Details of the structural defects and band structures were elucidated and correlated with their photoactivities for synthesized titania nanotubes. To examine the photocatalytic activities of as prepared and modified titania nanotubes, photoalytic oxidation of trimethylamine (N(CH<sub>3</sub>)<sub>3</sub>) gas was carried out under UV (254 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 TiO<sub>2</sub> nanotubes by controlled chemical treatment has not been known. These noble ultrahigh crystalline TiO<sub>2</sub> nanotubes can be applied as highly photoactive catalysts, supports, and advanced materials.

#### O9.7

**Electrochemical Synthesis and Characterization of Prussian Blue Nanostructures.** Chunglin Tsai<sup>2</sup>, Sathyajith Ravindran<sup>3</sup> and Cengiz Sinan Ozkan<sup>1</sup>; <sup>1</sup>Mechanical Engineering, University of California at Riverside, Riverside, California; <sup>2</sup>Electrical Engineering, University of California at Riverside, Riverside, California; <sup>3</sup>Chemical 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 multitallented properties of Prussian blue include 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) with electrodeposition in porous template using liquid mercury electrode. Several characterization techniques had been performed on the PBNT, including SEM, TEM, FTIR, and EDS. To exploit these Prussian blue nanotubes/nanowires (PBNT/PBNW), they were incorporated into micro/nano patterned electrochemical cell on silicon chip to build a miniaturized PB cholesterol/glucose bio-sensor. The PB cyclic voltammatic measurement confirmed the change of peak current and voltage according to the amount of 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 properties, 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.** Tsuyoshi Ueda<sup>1</sup>, Hideyuki Norimatsu<sup>1</sup>, Md.Mosharraf Hossain Bhiyan<sup>2</sup>, Tomoaki Ikegami<sup>3</sup> and Kenji Ebihara<sup>3</sup>; <sup>1</sup>Graduate School of Science and Technology, Electrical and Computer Science, Kumamoto University, Kumamoto, Japan; <sup>2</sup>Graduate School of Science and Technology, System and Information, Kumamoto University, Kumamoto, Japan; <sup>3</sup>Faculty of Engineering, Electrical and Computer Engineering, Kumamoto University, Kumamoto, Japan.

Carbon nanotube (CNT) is a promising material which has potential for applications to various nanotechnology devices owing to its unique features like high electrical conductivity, mechanical strength and large specific surface area. Recently, gas sensors using CNTs or carbon nano-fiber, which have extremely high sensitivity at a room temperature with fast response, have been reported. Being exposed to oxidizing gas like NO, NO<sub>2</sub> or O<sub>3</sub>, 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 O<sub>2</sub> and O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 of wavelength 248 nm, repetition rate 10 Hz, energy fluence 3 J/cm<sup>2</sup>. During PLD process the substrate temperature and the ambient gas pressure were kept at room temperature of 25 °C and 3.5x10<sup>-5</sup> Torr, respectively. The thickness and roughness of the films were modified by changing a number of ablation laser pulses from 1,000 to 36,000. 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 quartz reaction tube, Ar gas was used and its flow rate of 80 sccm 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 both the Si substrate and the sensor substrate. A diameter of CNTs was found 10–20 nm which tended to be proportional to the size of catalyst particle. The Sensitivity of CNT gas sensor was evaluated by measuring the electrical characteristic of the sensor. The sensor was exposed to one of the N<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub> gases of different concentration in a chamber. Resistance 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 thin film properties (i.e. orientation, density and Raman spectra) and sensitivity was investigated. Detail studies and the latest data will be presented at the symposium.

#### O9.9

**Study on the Synthesis of Carbon Nanotubes using the Catalyst Metal Deposited Carbon Cathode Electrode in a DC Arc Discharge Process.** Hyeon Hwan Kim and Hyeong Joon Kim; Material Science & Engineering, Seoul National University, Seoul, South Korea.

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 deposited at thicknesses between 2000 - 10,000 Å 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 & the 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 1nm were mainly detected in the soot collects. But using the Ti film, the SWNTs were not achieved. Besides the SWNTs, Multi wall carbon nanotubes (MWNTs) were also produced in the deposit collects regardless of the kind of catalyst metal. The outer diameters of MWNTs varied from several nanometers to tens of nanometers depending on the process conditions. The longer arc discharge time maintained at the same process current, the larger outer diameters MWNTs had. But the inner diameter variations were not significant according to the process conditions. From this result, we supposed that the forming mechanism of the inner and outer circle of CNT would be different. The concentration of catalyst in the final products was analyzed by Thermogravimetric Analysis (TGA). It showed that the catalyst concentration in the collect was gradually changed by the function of the arc plasma time. The collects which were gained in the initial stage of the process had higher metal concentration than the collects in the following or final stage due to the limited evaporation rate of the catalyst metal film on the carbon cathode electrode. At the lower metal concentration, the quantities of SWNTs were decreased but the quantities of by-products and MWNTs were increased. Through these results, the optimized catalyst metal concentration could be deduced for higher yields of SWNTs.

#### O9.10

**Preparation of Titanium Oxide and Metal Titanates as Powders, Thin Films, and Microspheres by Novel Inorganic Sol-Gel Process.** Andrzej Deptula<sup>1</sup>, Kenneth C. Goretta<sup>2</sup>, T.

Olczak<sup>1</sup>, W. Lada<sup>1</sup>, A.G. Chmielewski<sup>1</sup>, U. Jakubaszek<sup>1</sup>, Carlo Alvani<sup>3</sup> and Sergio Casadio<sup>3</sup>; <sup>1</sup>Institute of Nuclear Chemistry and Technology, Warsaw, Poland; <sup>2</sup>Argonne National Lab, Argonne, Illinois; <sup>3</sup>ENEA, C.R.E. Casaccia, Italy.

Titanium oxide and various titanates are being extensively studied as materials for advanced technologies, such as TiO<sub>2</sub> photocatalysts and supports for metallic catalysts, tritium breeders for fusion reactors (Li<sub>2</sub>TiO<sub>3</sub>), and cathodes for Li-based batteries (Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>).

Additionally, BaTiO<sub>3</sub> and its alloys are widely used in a variety of electronic applications. We report on a preparation procedure for these classes of compounds (including titanates based on Li, Na, K, Ba, or Sr), which utilizes a commercial and inexpensive solution of TiCl<sub>4</sub> and HCl. The main preparation steps consist of elimination of chloride anions by distillation with nitric acid, and addition of hydroxides of various metals for the titanates. The sols that were prepared were used to: - produce by a dipping technique thin films on metallic supports (Ni, Ag, Ti); - prepare irregularly shaped powders by evaporation of sols; - produce spherical powders (with particle diameters <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 to form the compounds by conventional solid-state reactions. The temperatures of formation could be further decreased by addition of ascorbic acid to the sols.

#### O9.11

**The effect of metal clusters on carbon nanotube based sensors.** Jeong-O Lee<sup>1</sup>, Byung-Kye Kim<sup>2,1</sup>, Hye-Mi So<sup>1</sup>, Hyunju Chang<sup>1</sup>, Ki-jeong Kong<sup>1</sup>, Youngmin Choi<sup>1</sup>, Ju-Jin Kim<sup>2</sup>, Noejung Park<sup>3</sup> and Beyong Hwan Ryu<sup>1</sup>; <sup>1</sup>Advanced materials Div., Korea Research Institute of Chemical Technology, Daejeon, South Korea; <sup>2</sup>Department of Physics, Chonbuk National Univ, Chonju, South Korea; <sup>3</sup>Department 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 clusters have been investigated. The source-drain current passing through an SWNT-FET coated with Pd nanoparticles showed no change over a range of gate voltages. Nevertheless, the magnitude of the current was still sensitive toward NO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub> exposure. The Pd nanoparticles coating the nanotube generated hole carriers, which either became diluted upon NH<sub>3</sub> or H<sub>2</sub> adsorption, or enhanced upon NO<sub>2</sub> adsorption. Unlike the Ohmic behavior demonstrated by SWNT-FETs coated with Pd nanoparticles, the transfer characteristics of SWNT-FETs coated with Al nanoparticles revealed Schottky barrier formations at the metal-nanotube contacts. Here, the conductance through the nanotube decreased, while the device sensitivity toward NO<sub>2</sub> and NH<sub>3</sub> 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.

#### O9.12

**EXAFS Study on Nanosized PtRu Catalyst for Direct Methanol Fuel Cell.** Hiroaki Nitami<sup>1</sup>, Takahiro Ono<sup>1</sup>, Yusuke Honda<sup>1</sup>, Takashi Nakagawa<sup>1</sup>, Takao A. Yamamoto<sup>1</sup>, Hideo Daimon<sup>2</sup> and Yukiko Kurobe<sup>2</sup>; <sup>1</sup>Graduate School of Engineering, Osaka University, Suita city, Osaka pref., Japan; <sup>2</sup>Development & 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 expected to be next generation's power source. 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 difference exists in arrangement of Pt and Ru atoms in PtRu catalyst showing different catalytic activity. 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. 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). Composition, crystallographic structure and morphology of PtRu catalyst were examined by XRF, XRD and TEM. Pt-L<sub>III</sub> edge EXAFS spectra of PtRu catalyst were obtained at the BL-7C beam line of KEK-PF. 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, however, did not find out a distinct difference between these two catalysts. EXAFS analysis found that there is 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 an associate catalyst for oxidation of CO which chemisorbs on active site of Pt. Based on bifunctional mechanism, it is preferred that Pt and Ru atoms exist contiguously each other for oxidation of CO by hydroxyl functional group generated on Ru. LSV measurement and EXAFS analysis revealed that PtRu catalyst in which 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 in 2 nm by addition of phosphorous (P). Effect of P addition on catalytic activity for methanol oxidation reaction is also discussed.

#### O9.13

**A Novel Carbon Material: Marimo Carbon.** Kiyoharu Nakagawa<sup>1</sup>, Mikka Nishitani-Gamo<sup>2</sup>, Hidenori Gamo<sup>3</sup>, Shigemitsu Hashimoto<sup>4</sup>, Toshiyuki Ishida<sup>4</sup> and Toshihiro Ando<sup>1</sup>; <sup>1</sup>National Institute for Materials Science (NIMS), Tsukuba, Japan; <sup>2</sup>Applied Chemistry, Toyo University, Kawagoe, Saitama, Japan; <sup>3</sup>Toppan Printing Co., Ltd., Sugito, Japan; <sup>4</sup>GEN-TECH, Inc., Yokohama, Japan.

We have developed a novel catalytic process to yield a novel carbonaceous material, named Marimo 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 supplied 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 supported metal catalysts in the temperature range from 525 to 700 °C to yield very thin carbon filamentous materials. No reaction can proceed without the diamond supported catalysts. The fine diamond powder played as a catalyst support and a nuclei for the carbonaceous deposits. Carbon nano filaments were produced onto the small catalyst 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 substrates, and formed a secondary structure like the Marimo. The Marimo carbons were formed to be spherical-ball shape which diameters were 1 to 10 micro meter in this study. The secondary diameter was relational to the reaction time. The marimo carbon has a large specific surface area and mechanical strength with a very low density and light weight. It is expected to be applied as a new catalysts support, a substrate for dielectric capacitors, a new electrode material for fuel cells, a new carbon component for complex composite materials.

#### O9.14

**Preparation and characterization of thin films by pulsed laser deposition for NO<sub>x</sub> gas sensor.** Md. Mosharraf Hossain Bhuiyan<sup>1</sup>, Tsuyoshi Ueda<sup>1</sup>, Keiji Shingu<sup>1</sup>, Tomoaki Ikegami<sup>2</sup> and Kenji Ebihara<sup>2</sup>; <sup>1</sup>Graduate School of Science and Technology, Department of Systems and Information, Kumamoto University, Kumamoto, Japan; <sup>2</sup>Department of Electrical and Computer Engineering, Kumamoto University, Kumamoto, Japan.

Tungsten trioxide (WO<sub>3</sub>) based materials as sensors for monitoring of environmental gases such as NO<sub>x</sub> have been developed for various potential applications. The sensing mechanism lies in the change 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 NO<sub>x</sub> 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 WO<sub>3</sub> thin films significantly. The gas sensors based on WO<sub>3</sub> thin films doped with different amount of platinum (Pt) or gold (Au) or palladium (Pd) or Ag were synthesized by KrF excimer pulsed laser deposition method with dc sputtering. The films were deposited on silicon, quartz and Al<sub>2</sub>O<sub>3</sub> substrate with Pt interdigital electrodes at various 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 1.5 × 10<sup>-5</sup> Torr. The targets (WO<sub>3</sub>, WO<sub>3</sub>-Pt, WO<sub>3</sub>-Au, WO<sub>3</sub>-Pd, WO<sub>3</sub>-Ag, Dowa, purity=99.99%, φ=30 mm) were ablated by KrF excimer laser (Lambda Physik LPX305icc, 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 300 mTorr, respectively during the deposition. The crystalline structure and crystallographic orientation of the prepared thin films were examined by the XRD (Rigaku RINT2000/PC) with Cu Kα radiation. The surface morphology and the structure of the films were observed by the AFM (Seiko

Instruments Inc. SPI3800N). The optical transmission of the prepared films was measured using a spectrophotometer (Ocean Optics). To evaluate the sensor property of the films, the electrical resistance of the WO<sub>3</sub> thin films was measured by a two-terminal resistance method in a chamber. The sensitivity of the WO<sub>3</sub> thin films was calculated from the resistance in the NO gas. The flow of NO gas was adjusted by a mass flow controller. The thin film sensors were heated 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<sub>3</sub> thin films gas sensors with doping (PGM or Ag) was found to be higher than that of pure WO<sub>3</sub> thin films gas sensors without doping. To improve the efficiency further we are trying to develop sensors based on WO<sub>3</sub> doped with SnO<sub>2</sub> and also SnO<sub>2</sub> 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 Shibasaki<sup>1</sup>, Hidenori Gamo<sup>2</sup>, Kiyoharu Nakagawa<sup>3</sup>, Toshihiro Ando<sup>3</sup> and Mikka Nishitani-Gamo<sup>1</sup>; <sup>1</sup>Applied Chemistry and Sensor Photonics Research Center, Toyo University, Kawagoe, Saitama, Japan; <sup>2</sup>Technical Research Institute, Toppan Printing Co. Ltd, Sugito, Saitama, Japan; <sup>3</sup>Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan.

We recently have developed a novel catalytic method for synthesizing a wide variety of carbon nanomaterials in the organic liquid (1). The method realized a simple, speedy, and high-purity growth of carbon nanotubes in alcohol liquids (2). In this study, Cobalt was used as a catalyst metal. In order to control of carbon nanomaterials, we investigated the relation between the growth conditions and the grown materials. The carbon nanomaterials, such as carbon nanotubes and fibers were grown in the alcohol liquid by the method under various growth conditions. The apparatus used in our experiments consists of a quartz chamber with outside cooling water. Methanol was used as the organic liquid. Catalyst metal was deposited on the silicon substrate with using a magnetron sputtering system. The Co-loaded silicon substrate was heated by applying a direct current through the substrate. The morphology of grown materials was observed by Scanning Electron Microscopy (SEM). The structure of grown materials was observed by Transmission Electron Microscopy (TEM). SEM observation revealed that the morphology of the grown carbon nanomaterials depended on the reaction temperature. Under the reaction temperature in the range from 600 to 700 °C, fibriform 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 fibriform carbon grown with a different thickness of the catalyst film. The more increase of the Co film thickness, the more thickens of filament diameter. The fibriform carbons grown with 1 nm thickness of Co have little coaxial follow channel. In contrast, the grown materials with 3 and 6 nm thickness of Co have coaxial follow channel; the deposits could be called as carbon nanotubes. The amount of supported catalyst affects structure of the grown fibriform carbon. A chemical and/or physical states of the catalyst is one of the effective parameter for the growth and structure of the grown materials. References 1) T. Ando, M. N.-Gamo, Y. F. Zhang, PCT/JP02/06235. 2) Y. F. Zhang, M. N.-Gamo, C. Y. Xiao, and T. Ando, Jpn. J. of Appl. Phys., 41, L408-L411 (2002).

#### **09.16**

**Functionalization of 3-D Structures for Grafting of Biological Molecules.** Cecile Oillic<sup>1</sup>, P. Mur<sup>1</sup>, E. Blanquet-Nicolas<sup>2</sup>, G. Delapierre<sup>1</sup>, F. Vinet<sup>1</sup> and T. Billon<sup>1</sup>; <sup>1</sup>CEA-DRT-LETI - CEA/GRE, Grenoble Cedex9, France; <sup>2</sup>LTPCM/ENSEEG/INPG, Saint Martin D'Heres Cedex, France.

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 critical 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 biological molecules 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 both. Moreover, due to the low amount of biological samples, the sensitivity and the reliability of detected signal become major problems. To achieve a high density of reactive functions, the use of a non-planar structure is investigated to increase the 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 to modify 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 stable bindings of amino-modified oligonucleotides 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 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 surfaces of 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 conformity 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; Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Gas sensors based on optical absorption changes in thin films are of interest for detection of various gases such as CO, NO, H<sub>2</sub>. 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 (1), showing an absorbance change in CO gas 70 times greater than those prepared by sputtering methods (2). Here we examine the effect of film microstructure and composition on CO gas sensing properties in order to identify the origin of the high sensitivity. Cobalt oxide films were prepared by PLD from a CoO 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 Zbroniec, Takeshi Sasaki and Naoto Koshizaki, Technical Digest of the 10th International Meeting on Chemical Sensors, Tsukuba, Japan (2004) p.358-359. 2) Masanori Ando, Tetsuhiko Kobayashi, Sumio Iijima and Masatake Haruta, J. Mater. Chem., 7 (1997) 1779-1783.

#### **09.18**

**Preparation of Cu-SiO<sub>2</sub> Nanoparticle and Study of Antibiotic Property.** Young Soo Kang and Young Hwan Kim; Chemistry, Pukyong, Pusan, South Korea.

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 Stober method by hydrolysis and condensation of TEOS in a mixture of ethanol with water, using ammonia as catalyst to initiate the reaction. These SiO<sub>2</sub> nanoparticles were dried at 100 °C. We measured the size of these nanoparticles with transmission electron microscopy (TEM). Second, Cu-SiO<sub>2</sub> nanoparticles were synthesized by reaction with CuCl<sub>2</sub> and SiO<sub>2</sub> nanoparticles at room temperature for 12 hrs. Results show silica nanoparticles of about 60 nm size with regularly deposited Cu nanoparticles. Cu-SiO<sub>2</sub> 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<sub>2</sub> nanoparticles applied to antibiosis.

#### **09.19**

**Thermally Grown Aligned Carbon Nanotubes on SiC Fibers for Electrochemical Applications.** Bill Logan Riehl<sup>1</sup>, Michael Check<sup>1</sup>, John Boeckl<sup>2</sup>, William Mitchel<sup>2</sup> and Elmo Blubaugh<sup>1</sup>; <sup>1</sup>Riehl-Check Industries, Beavercreek, Ohio; <sup>2</sup>Materials and Manufacturing Directorate, Air Force Research Laboratories, Fairborn, Ohio.

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 surface of macroscopically uniform dimension 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 partial charge transfer, have allowed aligned carbon nanotubes to be used in a very large range of detection mechanisms. These mechanisms include, but are not limited to impedance spectroscopy due to chemisorption of gases onto CNT arrays. This presentation will cover some of the work undertaken by Riehl-Check Industries and the Air Force Research Laboratories to utilize a radially grown CNT array on a conductive SiC substrate. The length of the CNT arrays grown vary significantly from those grown on a planar substrate, most likely due to better mass transport from the cylindrical substrate in comparison with the planar. The resulting CNT array is composed of single and multiwall CNTs with a dispersion of nano particles of graphitic carbon. This work includes, but is not limited to a traditional electrochemical study of the electrode made by the process in aqueous solution. Electrochemical species studied include ferricyanide, ferrocene, silver and platinum. It was found that the resulting sensor also displays an interesting pH response. The work described is leading to further development of the technology including fuel cells, bio-fuel cells, photovoltaic cells, pH sensors, LEDs and aqueous and vapor phase chemical detection.

#### **O9.20**

##### **Synthesis and Assembly of Mono and Bimetallic Nanoparticles for Sensing Volatile organic Compounds.**

Nancy N. Kariuki, Jin Luo and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

Bimetallic nanoparticles and their ensembles exhibit interesting electronic, optical, and chemical or biological properties due to bifunctional or synergistic effects. Several types of gold-based 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 composition and size controllability in a wide range has not been established. At the same time, little is known about assemblies of binary or ternary metal nanoparticle systems, 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 nanoscale properties of the bimetallic nanomaterials for chemical/biological sensing and catalytic applications. The synthesis of alkanethiolate-capped AuAg nanoparticles was carried out using a two-phase reduction of AuCl<sub>4</sub><sup>-</sup> and AgBr<sub>2</sub><sup>-</sup> both of which are, separately, first transferred into organic solution. The assembly utilizes the unique interparticle-linking chemistry of difunctional groups at Ag and Au sites for defining the interparticle chemistry. The nanostructured thin film assemblies were tested for sensing volatile organic compounds using chemiresistor transducers. Implications to the exploration of the mono and bimetallic nanoparticles for constructing sensing arrays and catalytic nanomaterials will also be discussed.

#### **O9.21**

##### **Abstract Withdrawn**

#### **O9.22**

##### **Magnetic Nanocomposite Films of High Temperature Polyimides.**

Sang-Hyon Chu<sup>1,2</sup>, Keun J. Sun<sup>1,2</sup>, Min Namkung<sup>2</sup>, Russell A. Wincheski<sup>2</sup> and Ruth H. Pater<sup>2</sup>; <sup>1</sup>National Institute of Aerospace, Hampton, Virginia; <sup>2</sup>NASA Langley Research Center, Hampton, Virginia.

The purpose of the present study is to develop magnetic nanocomposite films with excellent magnetic sensitivity, conformal capability, and material stability, by incorporating magnetic nanoparticles into high temperature polyimides developed at 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 resistance to moisture-induced damages. Such 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 wide 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 exploiting nanoparticles that are already prepared or 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 semiconducting nanocrystals, carbon nanotubes, high dielectric nanoparticles, 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 nanoparticles. The subsequent process of film fabrication and curing successfully produced free-standing 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 nanostructures of the magnetic films. FTIR spectroscopy and differential scanning calorimeter were used for characterizing 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.

#### **O9.23**

##### **Mechanochemical Synthesis, Structural Characterization and Visible Light Photocatalysis of TiO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> Nanocomposites.**

Sesha S. Srinivasan<sup>1</sup>, Jeremy Wade<sup>1</sup>, Nikolai Kislov<sup>1</sup>, Matthew T. Smith<sup>1</sup>, Elias Lee Stefanakos<sup>1</sup> and Yogi Goswami<sup>2</sup>; <sup>1</sup>Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida; <sup>2</sup>Solar 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. TiO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> has been selected among different alloys because of (i) its low band gap ~1.9 eV (ii) the nontoxicity of ZnFe<sub>2</sub>O<sub>4</sub> (iii) visible light absorption characteristics of ZnFe<sub>2</sub>O<sub>4</sub> due to its narrow band gap and (iv) not being susceptible to photoanodic corrosion. A mechanochemical synthesis approach using high energy milling is employed to prepare TiO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> under different experimental parameters and conditions. The as-milled nanocomposite materials are characterized with PXD, SEM and EDS procedures. The photocatalytic activity of TiO<sub>2</sub>/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites for the photodegradation of phenol under visible light irradiation has been studied systematically by UV-Vis spectrometer.

#### **O9.24**

##### **Study of Crystal Structure and Thermal Stability of Layered Sodium-Titanate Nanotubes.**

Paula Mendes Jardim<sup>1</sup>, Bojan Marinkovic<sup>1</sup>, Edisson Morgado<sup>2</sup>, Marco Antonio Santos de Abreu<sup>2</sup> and Fernando Rizzo<sup>1</sup>; <sup>1</sup>Materials Science and Metallurgy, PUC-Rio, Rio de Janeiro, RJ, Brazil; <sup>2</sup>PETROBRAS Research Center, Rio de Janeiro, RJ, Brazil.

Titanate 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 lepidocrocite-like structure, trititanate, hydrated tetratitanate and anatase. Studies on thermal and hydrothermal stability of single crystal titanate nanotubes are not so common in the literature. For instance, partially ion-exchanged nanotubes with nominal composition ascribed to H<sub>1.5</sub>Na<sub>0.5</sub>Ti<sub>3</sub>O<sub>7</sub> have been studied and their poor thermal stability reported with decomposition into anatase around 350°C [2]. In the present work Sodium-Titanate 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/H<sub>2</sub>O (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 Dispersive 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 are stable up to at least 600°C, transforming at around 700°C into Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>. TEM

images of the samples after heat treatment at 900°C gave evidence that Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> phase appeared in the form of nanorods. High Resolution Electron Microscopy, ED and XRD clearly showed that the nanotubes do not have the anatase structure. The other possible nanotube crystal structures are still under investigation. [1] T. Kasuga et al. *Langmuir* 14 (1998) 3160-3163. [2] R. Yoshida et al, *Materials Chemistry and Physics* 91 (2005) 409-416.

#### **09.25**

**Photocatalyst Application of ZnO Nanorods.** Jih-Jen Wu and Chan-Hao Tseng; Chemical Engineering, National Cheng Kung University, Tainan, 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-Hinshelwood model, the apparent 1st-order reaction rate constant is enhanced 2 order magnitudes. 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-meta/ZnO nanorod composites for MO degradation depend on the size and the density of the metal particles on the ZnO nanorods. The mechanism for the enhancement of the photocatalytic activity by forming nano-meta/ZnO nanorod composites will be discussed in this paper.

#### **09.26**

**Growth Behavior of One-dimensional, Single-crystalline Metal Oxide Nanostructures in Solution.** Bin Cheng and Edward T. Samulski; Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.

One-dimensional (1-D), metal oxide (ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>) nanostructures were synthesized in solution without using any surfactants or capping agents.<sup>1,2</sup> The aspect ratios (length/diameter) of these 1-D nanostructures can be tuned by delicately selected growth conditions (precursor concentrations, reaction temperature and time etc.). The synthesized nanostructures 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. [1] Bin Cheng, Edward T. Samulski, *Chem. Commun.* 2004, 986-987. [2] Bin Cheng, Joette M. Russell, Wensheng Shi, Lei Zhang, Edward T. Samulski, *J. Am. Chem. Soc.* 2004, 126, 5972-5973.

#### **09.27**

**Catalytic Effects and Characterization of Ni-based Catalysts Supported on TiO<sub>2</sub>-SiO<sub>2</sub> Xerogel for Oxidation of Acetaldehyde.** Jong-Woo Jeong<sup>1</sup>, Jong-Hui Park<sup>2</sup> and Chang-Seop Lee<sup>1</sup>; <sup>1</sup>Chemistry, Keimyung Univ., Daegu, South Korea; <sup>2</sup>Chemistry, 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 SiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub> as a xerogel followed by impregnating the Al<sub>2</sub>O<sub>3</sub> 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 NiAl<sub>2</sub>O<sub>4</sub> spinel structure at the calcination temperature of 673K in response to the steps with after- and co-impregnation of Al<sub>2</sub>O<sub>3</sub> powder in sol-gel process. The NiAl<sub>2</sub>O<sub>4</sub> could suppress the oxidation reaction of acetaldehyde by catalysts. The NiO is better dispersed on SiO<sub>2</sub>-TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> support than SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> 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 8wt.% Ni/TiO<sub>2</sub>-SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> showed the best conversion efficiency on acetaldehyde oxidation with 100 % conversion efficiency at 623K.

#### **09.28**

**Reactions of Organohalogenes with Zero-valent Sodium (Na<sup>0</sup>) Treated Faujasite 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. Na<sup>0</sup> treated faujasite zeolites decompose organohalogenes at room temperature. Using transmission IR, GC-MS, liquid 1H NMR and solid state 13C NMR, we report decomposition of methyl iodide, ethyl iodide and ethyl bromide. Methyl iodide in Na<sup>0</sup> activated NaX and NaY decomposes to form a framework stabilized methoxy species (O-CH<sub>3</sub>) with 13 C chemical shift of about 56 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 methoxy products were observed in activated NaX than in NaY. Ethyl iodide and bromide formed framework ethoxy and ethane 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 Hockey, 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 self-assembly from solution of nanoparticle-decorated latex 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 heating, the latex microspheres were removed to reveal a multiscale porous 3-dimensional structure composed of interconnected hollow nanoparticle microshells 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 micropipette. 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 50 nmol/mol (ppb) to 100 μmol/mol (ppm). Films composed of the smallest diameter (200 nm) nanoparticle microshells 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 (1.0 μm) nanoparticle microshells were the most sensitive to the 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 Souza<sup>1</sup>, Elton J. G. Santos<sup>1</sup>, Josue Mendes<sup>1</sup>, Odair P. Ferreira<sup>2</sup> and Oswaldo L. Alves<sup>2</sup>; <sup>1</sup>Fisica, Universidade Federal do Ceara, Fortaleza, Ceara, Brazil; <sup>2</sup>Quimica, 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 being the same for both dodecylamine- and Cu-intercalated VONTs. The spectra are characterized by peaks at 162, 250 and 910 cm<sup>-1</sup>. 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 V<sub>2</sub>O<sub>5</sub> oxide occurs through an intermediate compound that is isostructural to V<sub>2</sub>O<sub>5</sub> xerogel. The irreversibility of the decomposition process is confirmed by observing the color changes at the laser spot. The laser power density threshold needed for decomposing the VONTs into V<sub>2</sub>O<sub>5</sub> 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  $V_2O_5$  oxide. Our study allowed to establish the Raman signature of the VONTs and that this technique is powerful and useful as an ease/quick tool for probing VONTs samples.

#### **O9.31**

**Nanoscale characterization of Pd/TiO<sub>2</sub> catalysts and Ag/TiO<sub>2</sub> catalysts by electron holography.** Satoshi Ichikawa<sup>1</sup>, Tomoki Akita<sup>2</sup>, Kazuyuki Okazaki<sup>2</sup>, Koji Tanaka<sup>2</sup> and Masanori Kohyama<sup>2</sup>; <sup>1</sup>Organization for the Promotion of Research on Nanoscience and Nanotechnology, Osaka University, Toyonaka, OSAKA, Japan; <sup>2</sup>Research 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. Au/TiO<sub>2</sub> catalysts show the size dependence of the 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 TiO<sub>2</sub> supports. We applied electron holographic and high-resolution electron microscopic techniques to Au/TiO<sub>2</sub> catalysts, and found that the mean inner potential of Au particles supported on TiO<sub>2</sub> 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/TiO<sub>2</sub> catalysts is similar to that of the catalytic activity in Au/TiO<sub>2</sub> catalysts. In the present study, we examine the mean inner potential of Pd particles in Pd/TiO<sub>2</sub> catalyst and Ag particles in Ag/TiO<sub>2</sub> catalysts using electron holography and HRTEM. And we compare the results of the Pd/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> systems with our previous results of the Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> systems. In the case of the Pd/TiO<sub>2</sub> 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 higher 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/TiO<sub>2</sub> catalysts and Pt/TiO<sub>2</sub> catalysts. On the other hand, in the case of Ag/TiO<sub>2</sub> catalysts, the mean inner potential of Ag does not increase but slightly decrease though the size of the Ag particle decreases to under 2nm. It is considered that the difference of the work function is one of the reasons that the size dependence of Ag/TiO<sub>2</sub> system exhibits the peculiar behavior.

#### **O9.32**

**Catalytic and Physical Properties of Copper-Manganese Oxides Catalysts Supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for Toluene Oxidation.** Hye-Jin Kim<sup>1</sup>, Sung-Woo Choi<sup>2</sup> and Chang-Seop Lee<sup>3</sup>; <sup>1</sup>Environmental Science & Engineering, Graduated school, Keimyung Univ., Daegu, South Korea; <sup>2</sup>Environmental Science & Engineering, Keimyung Univ., Daegu, South Korea; <sup>3</sup>Chemistry, Keimyung Univ., Daegu, South Korea.

The catalytic incineration of toluene over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported copper-manganese oxides catalysts in the temperature range of 433-553K was investigated by employing a fixed bed flow reactor. The catalysts were characterized by BET surface area, 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. 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 Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> 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.** Woo Lee, Roland Scholz, Kornelius Nielsch 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 widely accessible electrochemical method for the preparation of arrays of metal 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 chemistry between Ag(I) and Sn(II) 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.,  $2Ag(I)(aq) + Sn(II)_{surface} \rightarrow 2Ag(0)_{surface} + Sn(IV)_{surface}$ ). 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]<sub>n</sub>) along the nanotube axes by employing sequential electrodeposition. We assume that the present electrochemical method for the 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 functional molecules (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 MFeOx (M = Cu, Fe, Mn, Ni, Zn) aerogels as magnetic nanoarchitectures.** Katherine Ann Pettigrew<sup>1,3</sup>, Jeffery W. Long<sup>1</sup>, Everett E. Carpenter<sup>2</sup>, Rhonda M. Stroud<sup>3</sup> and Debra R. Rolison<sup>1</sup>; <sup>1</sup>Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; <sup>2</sup>Chemistry, Virginia Commonwealth University, Richmond, Virginia; <sup>3</sup>Materials and Sensors Branch, Naval Research Laboratory, Washington, District of Columbia.

We have developed MFeOx (M = Cu, Fe, Mn, Ni, or Zn) nanoarchitectures 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 MFeOx 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 MFeOx, confirming that M(II) 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 nanostructures. Of particular interest will be the interaction of guest ions and molecules within the magnetic nanoarchitectures, with potential applications for sensing and separations. 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. Rolison, *J. Non-Cryst. Solids*, 350, 182 (2004). [2] A.E. Gash, T.M. Tillotson, J.H. Satcher, 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. Christman<sup>1,2</sup>, Michael V. Requa<sup>3</sup>, Vanessa D. Enriquez-Rios<sup>2</sup>, Paula Mendes<sup>1,2</sup>, Kimberly L. Turner<sup>3,4</sup> and Heather D. Maynard<sup>1,2</sup>; <sup>1</sup>California NanoSystems Institute, University of California Los Angeles, Los Angeles, California; <sup>2</sup>Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, California; <sup>3</sup>Mechanical Engineering, University of California Santa Barbara, Santa Barbara, California; <sup>4</sup>California 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 used in fabrication. As an alternative approach, we have recently developed a methodology for protein patterning using pH-responsive polymer films and photolithography. This technique uses poly(3,3'-diethoxypropyl methacrylate) (PDEPMA), which contains reactive acetal groups that hydrolyze to aldehydes in the presence of acid. Aldehydes easily react with aminoxy-functionalized compounds at neutral pH and can be reacted with amines via reductive amination. We first demonstrated micron scale protein patterning (18 x 18 micron features) using PDEPMA, the photoacid generator (PAG)

triphenylsulfonium triflate, and deep ultraviolet light ( $\lambda_{\text{max}}=248$  nm). In the current study, we examine the utility of PDEPMA for protein patterning at the sub-micron scale. PDEPMA plus the PAG diphenyliodonium-9,10-dimethoxyanthracene-2-sulfonate (DIAS) were spin-coated onto  $\text{C}_4\text{F}_8$  coated silicon wafers. Silicon wafers were treated with  $\text{C}_4\text{F}_8$  gas ignited into plasma in order to create a more hydrophobic 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 secs through a mask. The mask contained arrays of features ranging from the micron to sub-micron scale. Tapping mode 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 bound specifically to locations of light exposure, with minimal background staining. Due to the multiple binding sites on streptavidin for biotin, biotinylated ligands could then be attached to the arrays for use in enzyme linked immunosorbent assays. Alternatively antibodies could be functionalized with an aminoxy 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 Knez<sup>1</sup>, Miroslav Malešević<sup>2</sup>, Woo Lee<sup>1</sup>, Markus Liebscher<sup>2</sup>, Pia Myllymäki<sup>3</sup>, Matti Putkonen<sup>3</sup>, Kornelius Nielsch<sup>1</sup>, Lauri Niinistö<sup>3</sup> and Ulrich Goesele<sup>1</sup>; <sup>1</sup>Max Planck Institute of Microstructure Physics, Halle, Germany; <sup>2</sup>Max-Planck Research Unit for Enzymology of Protein Folding, Halle, Germany; <sup>3</sup>Laboratory 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 our porous structure, a monocrystalline arrangement of pore channels on a  $\text{cm}^2$ -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 thiol-capped active linker molecules and for titania membranes phosphate 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 luciferin. Due to 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 improved 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

**$\text{N}_2$  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  $\text{C}_2\text{H}_2$  gas flow ratio of 30 sccm. Fe catalysts were pre-deposited by RF sputtering system with RF power 150 W. Two kinds of as-grown CNTs were used to detect  $\text{N}_2$ : 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 or bundle was found to increase as which exposed to  $\text{N}_2$  environment, and to return back after the  $\text{N}_2$  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, with more effective grooves on the surface, provided more lower binding-force bind sites to absorb  $\text{N}_2$  molecules than the CNTs mat, which prominently has interstitial sites. A three-terminal electrical measurement would be further performed to clarify the characteristics of  $\text{N}_2$  absorption under different applied gate voltages.

### O9.38

**Nanoforest-linked amperometric immunosensors with nanomolar detection limit.** Sang Nyon Kim<sup>1</sup>, Xin Yu<sup>2</sup>, Fotios Papadimitrakopoulos<sup>1,2</sup> and James F. Rusling<sup>2</sup>; <sup>1</sup>Polymer Program, IMS, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Chemistry, University of Connecticut, Storrs, Connecticut.

Amperometric enzyme-linked immunoassays were developed based on vertically aligned arrays of single-wall carbon nanotubes (SWNT forests<sup>1</sup>) assembled on pyrolytic graphite electrode surfaces.<sup>2</sup> SWNT forests with high surface coverage and low amount of defects enhanced biosensor performance (3.5-fold sensitivity improvement), which was monitored by using nanotube-bound peroxidase enzymes. Mediator-free detection of  $\text{H}_2\text{O}_2$  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 carboxylated ends of nanotube forests. Non-specific binding was minimized by utilizing casin/detergent and a detection limit of  $75 \text{ pmol mL}^{-1}$  (75 nM) was achieved for human serum albumin (HSA) in unmediated sandwich immunosensors using horseradish peroxidase (HRP) labels. Much lower detection limit (c.a.  $1 \text{ pmol mL}^{-1}$  (1 nM)) was acquired by using hydroquinone, as a mediator, providing significantly better performance than alternative methods. 1. 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, (38), 9451-9452. 2. Yu, X.; Kim, S. N.; 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 Veith, Andrew R. Lupini, Sergey N. Rashkeev, Stephen J. Pennycook 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  $\text{SiO}_2$  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

**Localized Heating of Magnetic Nanoparticles for Biological Control.** Andy Wijaya<sup>1</sup> and Kimberly Hamad-Schifferli<sup>2</sup>; <sup>1</sup>Chemical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Biological Engineering Division, 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 (Hamad-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 ( $d = 3\text{-}10\text{nm}$ ) 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 Petkov and Chuan-Jian Zhong  
Thursday Morning, December 1, 2005  
Room 200 (Hynes)

### 8:15 AM O10.1

**Synthesis of Nanocrystalline N-Doped  $\text{TiO}_2$  for Photocatalytic Applications.** Kranthi Kumar Akurati<sup>1,2</sup>, Andri

Vital<sup>1</sup>, Thomas Graule<sup>1</sup> and Markus Winterer<sup>2</sup>; <sup>1</sup>High Performance Ceramics, EMPA, Swiss Federal Laboratories for Materials Testing and Research, Zurich, Zurich, Switzerland; <sup>2</sup>Nanoparticle Process Technology, Department of Engineering Sciences, University Duisburg-Essen, Duisburg, Duisburg, Germany.

Since photoinduced decomposition of water on TiO<sub>2</sub> electrodes was discovered, semiconductor based photocatalysts has attracted extensive interest. TiO<sub>2</sub> combines good electrical properties with high catalytic activity and excellent stability in many solvents over a wide range of pH. However, because of the wide band gap, TiO<sub>2</sub> does not absorb visible light which is a large part of the solar spectrum. So, any shift in the optical response of TiO<sub>2</sub> from the UV to the visible spectral range will have a profound positive effect on the photocatalytic efficiency of the material which 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 TiO<sub>2</sub> by feeding TiCl<sub>4</sub> precursor along with NH<sub>3</sub> 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 TiCl<sub>4</sub> 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 TiCl<sub>4</sub> 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 edge of TiO<sub>2</sub> to be shifted to the longer wavelength region and methylene blue 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 \*O10.2

##### 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 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. References 1.) Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A., "Chemistry and Properties of Nanocrystals of Different Shapes", *Chemical Reviews*, 2005, 105(4), 1025. 2.) Narayanan, R.; El-Sayed, M. A., "Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Nanoparticle Shape Dependence and Stability", 2005, *Journal of Physical Chemistry B*, 2005, in press.

#### 9:00 AM O10.3

##### Synthesis and Evaluation of Tunable Microcellular Catalytic Structures for Microreactor Applications. Haibiao Chen and Woo Y. Lee; Chemical, Biomedical, and Materials Engineering, Stevens Institute of Technology, Hoboken, New Jersey.

Microcellular 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 development, 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 skeleton was formed and the microspheres were removed to create interconnected cells defined by the silica skeleton structure. The structure and properties of the microcellular silica were tuned by systematically controlling three key parameters: cell size, cell interconnectivity and skeleton density. The mechanical stability, pressure drop, and mixing behavior were evaluated as functions of these three key parameters. Layer-by-layer self-assembly was used to infiltrate and immobilize a thin layer of sub-micrometer catalyst particles on the skeleton of the microcellular silica. Microreactors filled with the microcellular catalytic structures were used to carry out hydrogen peroxide synthesis, and were compared with packed-bed microreactors.

#### 9:15 AM O10.4

##### Nanocrystalline catalysts based on CeO<sub>2</sub>-ZrO<sub>2</sub> doped by praseodymium or gadolinium: synthesis and properties. Yulia V. Frolova, Natalya V. Mesentseva, Vladislav A. Sadykov, Galina M. Alikina, Anton I. Lukashovich, E. A. Paukshtis, E. M. Moroz, V. I. Zaikovskii, E. B. Burgina, V. V. Kriventsov and D. I. Kochubey; Borekov Institute of Catalysis, Novosibirsk, Russian Federation.

Ceria-zirconia-based systems are promising as components of three-way catalysts, catalysts of selective oxidation/autothermal reforming of hydrocarbons into syngas at short contact times, oxide ion conductors for oxygen sensors application and cathodes/anodes in solid oxide fuel cells. Doping this system with low-valence cations allows to stabilize this solid solution in hydrothermal conditions and tune the lattice oxygen mobility due to formation of oxygen vacancies or complex defects. In this work, nanocrystalline samples of Pr/Gdx(CeZr)(1-x)/2O<sub>2</sub> (x(Pr, Gd)=0.05-0.3) prepared by polymerized precursor (Pechini) route and calcined at 500°C were studied by using XRD, TEM, EXAFS, IR spectroscopy of lattice modes and adsorbed CO and NO, CH<sub>4</sub> and H<sub>2</sub> TPR. Pt was supported by an 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, IR of lattice modes and Raman spectroscopy. A higher degree of Pr cations segregation is reflected in the positive deviation in the dependence of the lattice parameter on x from the linear trend at x(Pr)=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=0.2. This is reflected in the minimum of the middle-temperature lattice oxygen mobility at this dopant content as revealed by CH<sub>4</sub> and H<sub>2</sub> TPR data. Hence, incorporation of dopants into the lattice of ceria-zirconia solid solution generates more complex defects than simple anion 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 supporting onto 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 980878 Projects.

#### 9:30 AM O10.5

##### Practical nanomaterials and nanostructures in electronics. Alan Rae, NanoDynamics Inc., Buffalo, New York.

A quiet revolution is occurring in electronics where nanometals have the ability to revolutionize adhesives and solders, nano oxides are revolutionizing fuel cell efficiency, and nanowires as well as nanotubes 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.

#### 10:15 AM O10.6

##### Nanostructured alumina doped TiO<sub>2</sub> ceramics for gas sensors. Young Jin Choi, Amit Bandyopadhyay and Susmita Bose; MME, WSU, Pullman, Washington.

Nanostructured TiO<sub>2</sub> 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 TiO<sub>2</sub> powders, pure as well as alumina doped TiO<sub>2</sub> had anatase phase. Dopant concentration was varied between 5 and 15 wt%. Particle size analysis showed below 100nm particles for pure TiO<sub>2</sub> as well as doped TiO<sub>2</sub> samples. Average particle size of doped powders was generally lower than the pure TiO<sub>2</sub>. The BET specific average 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 m<sup>2</sup>/gm. Uniaxially pressed compacts using these nanopowders showed an increase in

conductivity in the furnace air environment with increasing temperature. Al<sub>2</sub>O<sub>3</sub> doped TiO<sub>2</sub> sensor was found to be selective for CO sensing at an operating temperature of 600 °C. The presentation will discuss synthesis, processing and characterization of pure TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> doped TiO<sub>2</sub> based ceramic sensors.

#### 10:30 AM O10.7

##### **In-Situ Synchrotron X-Ray Studies of Structure-Property Relationships During Methanol Oxidation on Cu (001).**

Jeffrey A. Eastman, Dillon D. Fong, Paul H. Fuoss, Peter M. Baldo, Loren J. Thompson, Guangwen Zhou and Lynn E. Rehn; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

Copper-based catalysts are used in a number of industrial processes involving methanol production, methanol reforming to produce hydrogen, or methanol partial oxidation to synthesize formaldehyde. Oxygen on Cu surfaces is known to increase activity for methanol decomposition, but the possible effects of nanometer-sized Cu<sub>2</sub>O surface islands or oxygen-induced surface structures on the catalytic 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<sup>-7</sup> 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 25 to 1000 °C. We observe that exposure of the clean Cu surface to low controlled partial pressures of oxygen (pO<sub>2</sub>) results in the formation of either a c(2x2) or a (2sqrt(2)xsqrt(2))R45° surface reconstruction, depending on temperature. With increasing pO<sub>2</sub>, Cu<sub>2</sub>O nano-islands nucleate and grow. We observe that the equilibrium phase boundary between Cu and Cu<sub>2</sub>O nanoparticles 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 structural dependence of the catalytic activity for methanol oxidation will also be discussed.

#### 10:45 AM O10.8

**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<sup>1</sup>, Yulia V. Frolova<sup>1</sup>, G. M. Alikina<sup>1</sup>, A. I. Lukashevich<sup>1</sup>, R. V. Bunina<sup>1</sup>, E. M. Moroz<sup>1</sup>, V. A. Rogov<sup>1</sup>, V. I. Zaikovskii<sup>1</sup>, A. V. Ishchenko<sup>1</sup>, V. V. Kriventsov<sup>1</sup> and N. Orlovskaya<sup>2</sup>; <sup>1</sup>Borckov Institute of Catalysis, Novosibirsk, Russian Federation; <sup>2</sup>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 separation and syngas generation. 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 comprised of doped ceria and rare-earth manganite phases. The approach is based on the modification of polymerized precursor (Pechini) route with fixing all constituting cations in the citric acid-ethylene glycol polyester matrix followed by its burning and calcination. Due to a limited solubility of Mn and Ln 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 =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. Evolution of the phase composition and real 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 ceria lattice is confirmed by increased unit cell size. Some spatial variation of the elements distribution between domains is revealed by EDX. This agrees with observed Raman bands at ~220, ~450 and ~580 cm<sup>-1</sup> 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 disordering of Ce-Me and Mn-Me coordination spheres revealed by EXAFS can be due to both nanosize effect and incorporation of doping cations into fluorite and perovskite lattices. The lattice oxygen mobility and reactivity estimated by O<sub>2</sub> TPD, H<sub>2</sub> and CH<sub>4</sub> TPR increase with the temperature of nanocomposites sintering due to improved percolation. This is confirmed by a high electronic and ionic conductivity measured for

sintered pellets. A high rate of methane and decane combustion in the 600-800 °C temperature range by the lattice oxygen of nanocomposites containing a mixture of rare-earth cations makes them promising 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 O10.9

**Ultrafast Pd/AAO Nanowell Hydrogen Sensor.** Jianjiang Lu, Shufang Yu and H. Hau Wang; Argonne National Lab, Argonne, Illinois.

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 short-term anodization of aluminum metal. The nanowell structure is made of shallow wells that were oriented in a hexagonally closed packed 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. Work at Argonne National Laboratory as well as measurements with FESEM carried out at EMC 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 O10.10

**The Electrosynthesis and Evaluation of WO<sub>3</sub> Nanowires for Chemical Microsensor Applications.** Kurt D. Benkstein and Steve Semancik; CSTL, National Institute of Standards and Technology, Gaithersburg, Maryland.

Nanowires have been attracting significant interest in nanoelectronics 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<sub>3</sub> (a material particularly responsive to NO<sub>x</sub> 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<sub>3</sub> nanowire fabrication as well as on their efficacy as the active material in conductometric chemical microsensors. Production of WO<sub>3</sub> nanowires was effected via template-directed electrosynthesis from solutions of W<sub>2</sub>O<sub>11</sub><sup>2-</sup> in track-etched polycarbonate membranes (d<sub>pore</sub> = 100 nm). The nanowires were characterized by optical and scanning electron microscopies, which showed that the nanowires were ~2.5 μm long and varied from 125 nm to 175 nm in diameter. Initial studies on 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 properties and response characteristics to be rapidly measured between 20 °C and 480 °C. Comparisons were made between the nanowires and WO<sub>3</sub> particulate films prepared by calcination of H<sub>2</sub>WO<sub>4</sub>. Both types of WO<sub>3</sub> films were evaluated as conductometric sensor materials for several target analytes, including NO<sub>2</sub> and methanol, in air-based background environments.

#### 11:30 AM O10.11

**Fabrication and electrical characterization of gas sensors based on tailored, tin oxide nano-particle.**

Tim Patrick Huelser<sup>1,2</sup>, Pascal Ifecho<sup>2</sup>, Hartmut Wiggers<sup>2</sup> and Axel Lorke<sup>1</sup>; <sup>1</sup>Institute of physics, University Duisburg-Essen, Duisburg, Germany; <sup>2</sup>Institute of combustion and gas dynamics, University Duisburg-Essen, Duisburg, Germany.

Rutile tin oxide (SnO<sub>1.7</sub>) nano-particles with mean diameter of 7 nm were synthesized in a low-pressure, H<sub>2</sub>/O<sub>2</sub>/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 capacitors were fabricated on an insulating 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 deposited particles was investigated under N<sub>2</sub> atmosphere and as well as under synthetic air

in the temperature range between 323 K and 503 K. For particles on inter-digital capacitors with a distance and width of 1 micron, two different contributions to overall impedance were determined under N<sub>2</sub> 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 N<sub>2</sub> atmosphere, this third 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 RCs 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. Our findings, particularly the additional detectable transport mechanism under oxidizing atmosphere open new routes for low temperature oxygen-sensing devices based on tin oxide nano-particles.

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

#### 1:30 PM O11.1

**Raman-based Nanostructured Sensors.** Maier S. Amer<sup>1</sup> and John F. Maguire<sup>2</sup>; <sup>1</sup>Mechanical & Materials Eng., Wright State University, Dayton, Ohio; <sup>2</sup>Materials & 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 meso-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 accurate 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 nanospheres 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

**Fabrication of Highly-ordered and Densely-spaced Silicon Nano-needle Arrays for Bio-sensing Applications.** Aijun Yin and Jimmy Xu; Engineering, Brown University, Providence, Rhode Island.

For intracellular sensing is highly desirable to form small (nanometer-scale), long (micrometer-scale), strong, and electrically active but chemically inert probing needles. Such nano-needles are challenging to fabricate by traditional methods. Moreover, for most applications, these nano-needles need to be mechanically anchored in and electrically interfaced with a solid micro (or macro) base. For the ease of integration with control electronics, the solid base is preferably to be silicon. Furthermore, for intracellular probing and explorations, these probing nano-needles 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-needles 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-needles 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 that is kept long enough to allow the formation of the desired array of silicon nano-needles of ~30nm in diameter and ~4um in length

#### 2:00 PM \*O11.3

**Synthesis, Characterization, and Magnetic Properties of Dendrimer-Encapsulated Iron, Cobalt, and Nickel Nanoparticles Containing <150 Atoms.** Richard M. Crooks and Marc R. Knecht; Chemistry, Texas A&M, College Station, Texas.

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 and stoichiometric amounts 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 Fe, Co, and Ni and containing 147 and 55 atoms were prepared. The resulting materials were nearly monodisperse in size ( $< \pm 0.3$  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 dependent 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.** Swanand D. Patil<sup>1,2</sup>, Anjum Mehta<sup>3</sup>, Hyoungseok Bang<sup>4</sup>, Hyoung J. Cho<sup>2</sup> and Sudipta Seal<sup>1,2</sup>; <sup>1</sup>Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida; <sup>2</sup>Department of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, Florida; <sup>3</sup>Department of Electrical Engineering, University of Central Florida, Orlando, Florida; <sup>4</sup>Creol, College of Optics and Photonics, University of Central Florida, Orlando, Florida.

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 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 particle size of 3-5nm with no agglomeration. A 3 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 technique to obtain the working potential. Flow of hydroxyl ions was measured for varying concentrations of the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution. A direct co-relation between the sensor signal and the (H<sub>2</sub>O<sub>2</sub>) concentration was observed. The X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of both, Ce<sup>3+</sup> and Ce<sup>4+</sup>, 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 Ce<sup>3+</sup> to Ce<sup>4+</sup>. Due to various surface chemical reactions the nanocrystalline ceria goes back to Ce<sup>3+</sup> oxidation state. These ongoing reactions in opposing directions ensure continuous regeneration of Ce<sup>3+</sup> ions, which aids in the longevity of the sensor. Compared to the previously developed H<sub>2</sub>O<sub>2</sub> sensors, nanocrystalline cerium oxide's regenerative property (Ce<sup>3+</sup> → Ce<sup>4+</sup> → Ce<sup>3+</sup>) 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.

Adsorbed 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 rapid 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, the individually addressable, 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). Most prior NIST microsensor work has focused upon the detection properties of SnO<sub>2</sub> or TiO<sub>2</sub> 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; for example, SnO<sub>2</sub> films grown from anhydrous tin nitrate precursor exhibit higher overall conductance and better dynamic range for detection of alcohols, while TiO<sub>2</sub> grown from titanium tetraisopropoxide (TTIP) demonstrates higher sensitivity to water vapor. We have expanded upon the performance orthogonality of this pair of oxides via simultaneous and layer-by-layer co-deposition of stannia and titania, ruthenium doping of oxide films via co-deposition of triruthenium dodecacarbonyl, and deposition of SnO<sub>2</sub> and TiO<sub>2</sub> 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 in tandem with temperature-dependent response 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.

#### 3:15 PM \*O11.6

**Fabrication and Characterization of Nanowire Bridges for Bio-Electronic Switches.** Robert J. Hamers, Chemistry, University of Wisconsin-Madison, Madison, Wisconsin.

We have investigated the use of nanowires bridging between 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, only slightly larger than many nanowires of interest. Measurements on nanowires show that the electrical response includes contributions from the capacitance associated 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 Gao<sup>1</sup>, Zhimou Yang<sup>1</sup>, Keming Xu<sup>2</sup>, Hongwei Gu<sup>1</sup> and Bing Xu<sup>1,2</sup>;

<sup>1</sup>Chemistry, The Hong Kong University of Science and Technology, Hong Kong, NA, Hong Kong; <sup>2</sup>Bioengineering 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 (with the sizes of 1-5 μm) in biological separation or 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 present the surface chemistry and 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 Crosslinked Dendrimer Metal Complexes by SPR/Potentiometry.** 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 highly toxic organophosphate nerve agents. Picomolar detection and specific recognition of Pinacolyl methylphosphonate (PMP) and Methyl phosphonic acid (MPA), the degradation product of nerve agent was achieved with a combined surface plasmon resonance (SPR) and potentiometry set-up. A modified PAMAM carbazole/Cu<sup>++</sup> dendrimer and its electropolymerization with SAM-carbazole was used as an active host matrix for trapping nerve agent analogs. The ultrathin films were used to study the anchoring of nerve agents via non-covalent interactions. The carbazole to amine ratio was optimized to ensure that free primary amines are left to interact with the analyte and also the copper ions present in the system which further enhanced the selectivity. To enhance the stability, robustness, and porosity in the film, it was necessary to crosslink the carbazole as a conjugated polymer moiety. The adsorption kinetics was monitored by using an in-situ SPR/potentiometric set-up.

#### 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 nanoparticles structures were generated by coating metals on the end of optical fibers, overcoating 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 Chemistries.** 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 sensing technologies. As a result, the IOC sensor technology is well suited for field use by non-technical personnel or for operation as an unattended 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 metallic shell that is reactive with specific chemical species. In doing so, nGimat has demonstrated the basic concept and its application to 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 ppbv 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, depositing 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 materials can be used 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 H<sub>2</sub>S, that index changes to approximately 1.64. In the future, nGimat anticipates even more dramatic sensitivity enhancement through the use of nanoparticles tailored to specific sizes.



SESSION O12: Poster Session: Nanoparticles and Nanostructures in Sensors and Catalysis IV  
Chairs: Nicholas Kotov and Chuan-Jian Zhong  
Thursday Evening, December 1, 2005  
8:00 PM  
Exhibition Hall D (Hynes)

### O12.1

**Self-signal amplifying bio-/synthetic hybrid sensory polymers for fast DNA detection.** Kangwon Lee<sup>1</sup>, Jae Cheol Cho<sup>1</sup>,

Ching-Chin Pun<sup>2</sup>, Jean Marie Rouillard<sup>2</sup>, Erdogan Gulari<sup>2</sup> and Jinsang Kim<sup>1,2,3</sup>; <sup>1</sup>Materials science and engineering, University of Michigan, Ann Arbor, Michigan; <sup>2</sup>Chemical engineering, University of Michigan, Ann Arbor, Michigan; <sup>3</sup>Biomedical 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-signaling property, and easy fabrication without the PCR amplification and the fluorescence labeling of analyte DNA. The long term application of the proposed technology could be the development of a self-sustained field detection device for bio-threat monitoring and diagnostic screening of gene-related diseases. Our bio-/synthetic hybrid sensory polymers have a conjugated polymer 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 beacons 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 discussed.

### O12.2

**Third-Order Nonlinear Optical Properties in Dendrimer Nanocomposites.** Ying Wang, Ted Goodson and Xie Xingbin; Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

Dendrimer metal nanocomposites are promising materials for optoelectronic devices and catalysis. The coupling of organic chromophores and metal nanoparticles in a hybrid structure may offer new and enhanced nonlinear optical (NLO) properties. To this aim we have investigated chromophore-functionalized dendrimer metal nanocomposites. In this presentation, the synthesis of a rhodamine-functionalized PAMAM dendrimer as well as metal nanocomposites prepared with this dendrimer will be described. Degenerate-four-wave-mixing (DFWM) measurements were used to characterize the third-order nonlinear optical properties of the fabricated materials. An enhancement of third-order NLO susceptibility was obtained for the chromophore-functionalized dendrimer metal nanocomposites. Specific interactions of the dipole moment of the attached chromophores with the metal particle surface plasmon resonance are suggested to contribute to the observed enhanced NLO response of the functionalized dendrimer metal nanocomposites. Time-resolved spectroscopy is used to probe the mechanism of energy transfer processes in these materials. These results provide an insight into how certain organic/inorganic hybrid structures affect the NLO response and may play an important role in their use in photonics. References 1. Ispasoiu, R. G.; Balogh, L.; Varnavski, O. P.; Tomalia, D. A.; Goodson, T. Large Optical Limiting and Ultrafast Luminescence Dynamics from Novel Metal-Dendrimer Nanocomposite Materials, *J. Am. Chem. Soc.* 2000, 122, 11005-11006. 2. West, R.; Wang, Y.; Goodson, T. Nonlinear Transmission Investigations in Gold Nanostructured Materials, *J. Phys. Chem.* 2003, 107 (15): 3419-3426. 3. Varnavski, O.; Mohamad, M.; El-Sayed, M.; Goodson, T. Relative Enhancement of Emission in Gold Nanorods, *J. Phys. Chem.* 2003, 107 (14): 3101-3104. 4. Goodson, T.; Varnavski, O.; Wang, Y. Optical Properties and Applications of Dendrimer Nanocomposites, *Inter. Rev. of Phys. Chem.*, 2004, 23, 109-150. 5. Goodson III T., Optical Effects Manifested in Dendrimer Metal Nanocomposites, in *Dendrimers and Other Dendritic Polymers*, Edited by J. M. J. Frechet and D. A. Tomalia (Wiley), 70, 2001.

### O12.3

**Tungsten Nanowires and Microducts by Plasma Treatment of Thin Tungsten Films.** Prahalaad M. Parthangal<sup>2</sup>, Richard E. Cavicchi<sup>1</sup>, Christopher B. Montgomery<sup>1</sup>, Shirley Turner<sup>1</sup> and Michael R. Zachariah<sup>2,1</sup>; <sup>1</sup>Chemical Science and Technology Laboratory, National Institute of Standards & Technology, Gaithersburg, Maryland; <sup>2</sup>Mechanical Engineering, University of Maryland, College Park, Maryland.

We report on the growth of nanowires and unusual hollow microducts 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 H<sub>2</sub> was crucial in growing these nanostructures as was trace quantities of oxygen necessary to form a volatile tungsten species. To verify the role of H<sub>2</sub> as reducing agent rather than as an agent for creation of a WH<sub>x</sub> species, we replaced the H<sub>2</sub> 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 specific operating conditions hollow microducts having edge lengths ~ 0.5 μm and lengths between 10-200 μm were observed on treated tungsten films. Preferential restructuring of the film surface into nanowires or microducts 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 in air, exhibited capability of sensing trace quantities of nitrous oxides (NO<sub>x</sub>).

### O12.4

**Ab Initio Study of Helical Silver Single-Wall Nanotubes and Nanowires.** Shelly L. Elizondo 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 controlling the size and shape of silver and gold nanostructures 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 rolling up a triangular sheet of silver atoms and mapping the atoms onto the surface of a cylinder, comparable to rolling up a graphite sheet for a carbon nanotube. 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 Bennett<sup>1</sup>, Anastasios John Hart<sup>2</sup> and Robert E. Cohen<sup>1</sup>; <sup>1</sup>Chemical Engineering, MIT, Cambridge, Massachusetts; <sup>2</sup>Mechanical Engineering, MIT, Cambridge, Massachusetts.

Here we report a general route that utilizes block copolymer micelles as a means to create tunable inorganic nanocluster arrays which 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 strategies we use to vary these inorganic nanocluster arrays include the variation of the molecular weight of PS-*b*-PAA, the variation of the amount of metal loaded into the micellar solution, the addition of PS homopolymer into the micellar solution, and the mixing of different micellar solutions. Through these routes, we demonstrate varying the diameter of the inorganic nanoclusters from 4.7 nm to 16 nm and the areal density from  $6 \times 10^{10}$  nanoclusters per  $\text{cm}^2$  to  $6.5 \times 10^9$  nanoclusters per  $\text{cm}^2$ . 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 nanocluster arrays (size, center-to-center spacing, and density) as well as the reactor growth conditions. Using our approach we are also able to create arrays of metal nanoclusters containing multiple metal species, with each nanocluster containing either one or both of the metal species, depending on the sequence of processing conditions employed. We use this route to create nanoclusters that contain binary mixtures of metal species, and we examine their ability to catalyze carbon nanotube growth as we vary the composition of metal species within the nanoclusters.

#### **O12.6**

##### **In situ SAXS of Zeolite Microwave Hydrothermal Synthesis.**

Geoff Allen Tompsett<sup>1</sup>, Curt Conner<sup>1</sup>, Bernard Panzarella<sup>1</sup>, Sigfrid Yngvesson<sup>2</sup>, Fan Lu<sup>2</sup> and Keith Jones<sup>3</sup>; <sup>1</sup>Chemical Engineering, University of Massachusetts, Amherst, Massachusetts; <sup>2</sup>Electrical Engineering and Computer Science, University of Massachusetts, Amherst, Massachusetts; <sup>3</sup>Environmental Sciences, Brookhaven National Lab, Upton, New York.

The microwave hydrothermal synthesis of silicalite zeolite was monitored in situ using 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 stub tuners on the coax adapter end and also four waveguide tuning stubs at the opposite end of the waveguide. A reflector plate with a 38 mm hole was bolted between the coax adapter and the waveguide section and a copper plate was attached to the end of the waveguide as a short. The short creates a resonant waveguide cavity that can be tuned to obtain a peak frequency while maximizing the Q factor. Microwave power up to 300 W was supplied by a SAIREM generator via a coax connection. A sample port in the waveguide section allowed a thin-walled glass sample vial to be held in the microwave field. The sample vial was sealed with a fiber optic temperature probe used for monitoring the temperature. Silicalite zeolite precursor solutions of tetraethyl orthosilicate, tetrapropylammonium hydroxide and water were heated temperatures between 373 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 silicalite zeolite formation was successfully monitored and the analysis of 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 patterns obtained from a silicate precursor solution reacted at 393 K for 120 minutes. Fig. 1 SAXS of silicalite solution at 393 K with varying times

#### **O12.7**

**Creating nanostructures with controllable sidewall profile for mechanical sensor 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, in "bottom-up" techniques, it is difficult to arrange the structures in a desired pattern; while in "top-down" 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 vertical sidewall, and (2) a laterally suspending 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 lifted off, serving as the mask for the subsequent etching. A brief reactive ion etching (CF<sub>4</sub>/O<sub>2</sub>) 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 under such low pressure, the bottom oxide was rapidly removed while the sidewall 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, with a few  $\mu\text{m}$  in height. In the fabrication 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 base substrate. The sensitivity can be controlled by adjusting 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 forces occurring in a biological system, which range from a few  $\mu\text{N}$  down to pN, or less.

#### **O12.8**

**Core Size Effect of Monolayer-Protected Colloids on Chemiresistor Sensors.** Haick Hossain 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 chemically the inter-particle distance, and thereby obtain nearly uniform inter-particle distances in the composite films. This 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 metal-capped thiols can be correlated with the core size. These data demonstrate that the structure and reactivity of metal-capped alkythiols 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 chemiresistor sensors 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 maximums at ca. 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 (drift 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-biasing method which captures sensor response variability 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 O13.7

#### **O12.10**

**Molybdenum Sulfide Nanowires-Containing Catalyst: Tailoring the Selectivity by controlling the structure.**

Alejandra Camacho Bragado<sup>1</sup>, Miguel Jose Yacaman<sup>2,1</sup> and Gabriel Alonso<sup>3</sup>; <sup>1</sup>Texas Materials Institute, University of Texas at Austin, Austin, Texas; <sup>2</sup>Chemical Engineering, University of Texas at Austin, Austin, Texas; <sup>3</sup>Ingenieria Ambiental, CIMAV, Chihuahua, Chihuahua, Mexico.

We present preliminary results on the catalytic activity of nanostructured molybdenum sulfide. The bulk catalysts were prepared by sulfidation of molybdenum trioxide nanoribbons. The structural analysis of the resulting material was carried out by X-ray diffraction (XRD), scanning electron microscopy and transmission electron microscopy. Sulfides prepared by the method explored here are morphologically different to commercial MoS<sub>2</sub> (molybdenite) or

poorly crystalline MoS<sub>2</sub>. XRD and electron diffraction showed the presence of two phases, molybdenum dioxide and molybdenum disulfide, indicating that the sulfidation is not complete and the final product is constituted by a molybdenum dioxide 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. Those 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 well electron energy loss spectra of both, 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 are 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**

**Electrosprayed 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 electrosprayed onto heated substrates to obtain nano-crystalline thin films in order to improve the stability and sensitivity of MoO<sub>3</sub> and WO<sub>3</sub>. For gas sensing applications, specific crystalline phases are required with grain size stability at the operating temperatures of 200-500 oC. Traditional sol-gel processing results in poor adhesion and cracking of the metal oxide films formed and grain growth at sensing temperatures. In this process, MOX sol-gels were electrosprayed 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 electrosprayed MOX thin films are presented in this paper

#### **O12.12**

**Nanoelectrode for anodic stripping analysis of heavy metals.** Gil Ho Hwang, Jae Woong Choi, Seok Joon Hong, Won Kyu Han and Sung Goon Kang; Materials Sci. & Eng., Hanyang Univ., Seoul, South Korea.

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 materials 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.

#### **O12.13**

**Incorporation of tin oxide within mesoporous silica materials and their use for gas sensor applications.** Sinue Gomez<sup>1</sup>, Josanel Villegas<sup>1</sup> and Steven L. Suib<sup>2,1,3</sup>; <sup>1</sup>Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Chemical Engineering, University of Connecticut, Storrs, Connecticut.

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 resistivity sensors for reducing gases. In order to achieve further miniaturization of sensing systems we have focused our research on the development of metal oxides materials, 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 M41S 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-48 and MCM-41. The materials have been characterized by XRD, N<sub>2</sub> sorption, and HRTEM. The host materials maintain their structure and high surface area (700-1000 m<sup>2</sup>/g) after incorporation of the oxide. DC conductivity experiments were performed under different reducing gases (CO, NO<sub>x</sub>, H<sub>2</sub>) at temperatures above 573 K to test the response of the Sn-containing

mesoporous silica materials for sensor applications.

#### **O12.14**

**Particle Size Control of Cryptomelane Nanomaterials by Using H<sub>2</sub>O<sub>2</sub> in Acidic Conditions and Their Catalytic Applications.** Josanel C. Villegas<sup>1</sup>, Luis J. Garces<sup>2</sup>, Sinue Gomez<sup>1</sup>, Jason P. Durand<sup>2</sup> and Steven L. Suib<sup>2,1,3</sup>; <sup>1</sup>Materials Science, University of Connecticut, Storrs, Connecticut; <sup>2</sup>Chemistry, University of Connecticut, Storrs, Connecticut; <sup>3</sup>Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Manganese oxide octahedral molecular sieve (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 green reduction of KMnO<sub>4</sub> by H<sub>2</sub>O<sub>2</sub> under acidic conditions. An acetate-containing buffer solution and HNO<sub>3</sub> 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, potentiometric titration, TGA, TPD, and N<sub>2</sub> sorption analyses. Particle sizes of the manganese oxide nanomaterials were tailored by varying concentration of H<sub>2</sub>O<sub>2</sub> 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.** Claudiu 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 microelectronics 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 sensing 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 amorphisation 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 sensors to various concentration 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 migrating and forming island-like surface nanostructures 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 AAMURI Center for Advanced Propulsion Materials under the contract number NAG8-1933 from NASA. \*\* Corresponding author: Tel.: 256-372-5895; Fax: 256-372-5868; Email: claudiu@cim.aamu.edu

#### **O12.16**

**The Effect of Substrate and Catalyst Properties on the Growth of Multi-Wall Carbon Nanotube Arrays.** Sudheer Neralla<sup>1</sup>, Sergey Yarmolenko<sup>1</sup>, Vesselin Shanov<sup>2</sup>, YeoHeung Yun<sup>3</sup>, Mark J. Schulz<sup>2</sup> and Jag Sankar<sup>1</sup>; <sup>1</sup>Mechanical and Chemical Engineering, North Carolina A&T State University, Greensboro, North Carolina; <sup>2</sup>Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio; <sup>3</sup>Mechanical, Industrial and Nuclear Engineering, Smart Materials 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 C<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>-Ar-H<sub>2</sub>O 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 this study. In order to optimize 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 directions on a single substrate 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 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, and the presence of the silica layer on the growth and quality of the multi wall CNT were studied. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) were employed to characterize the morphology and the microstructure of the catalytically active surface. 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 Al<sub>2</sub>O<sub>3</sub> have a tremendous impact on the nanotube growth rate, alignment, and diameter, and need to be balanced to grow long MWCNT arrays.

#### **O12.17**

##### **Atomistic Simulations of Nanoporous Anodic Aluminum Oxide.** Shashishekar P. Adiga<sup>1</sup>, Peter Zapol<sup>1,2,3</sup> and Larry A.

Curtiss<sup>1,2</sup>; <sup>1</sup>Materials Science Division, Argonne National Laboratory, Argonne, Illinois; <sup>2</sup>Chemistry Division, 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 planar and concave amorphous alumina surfaces. We will discuss the effect of pore radius on the surface structure of amorphous alumina 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 oxide semiconductor, has been investigated for transistors, electrode materials, solar cells and gas-sensing devices. For gas sensors, we have grown tin oxide into SiO<sub>2</sub> opal structures by chemical vapor deposition from a tin tert-butoxide precursor. After growing, the infill was shown to be SnO<sub>2-x</sub>, 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 homogeneously deposited within the opal structure. Afterwards the glass template was removed by chemical etching, giving rise to an inverse opal. The SnO<sub>2</sub> and inverse SnO<sub>2</sub> 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**

##### **Surface electronic states in three-dimensional SnO<sub>2</sub> nanostructures.** S. O. Kucheyev, T. F. Baumann, P. A. Sterne, Y. M. Wang, T. van Buuren, A. V. Hamza, L. J. Terminello, J. H. Satcher and T. M. Willey; Lawrence Livermore National Laboratory, Livermore, California.

Ultralow-density monolithic SnO<sub>2</sub> nanostructures (aerogels) are synthesized using the epoxide-initiated gelation method. The as-prepared aerogels are comprised of a continuous network of interconnected, randomly oriented crystalline (rutile) SnO<sub>2</sub> nanoparticles ~3-5 nm in size with a high surface area of ~400 m<sup>2</sup>/g. The electronic structure of these aerogels is studied by soft x-ray absorption near-edge structure (XANES) spectroscopy. High-resolution O K-edge and Sn M<sub>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, and β-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 presence of undercoordinated surface atoms not only affects 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 surface 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> nanostructures. This work was performed under the auspices 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.** Vesselin Shanov<sup>1</sup>, Yun Yeo-Heung<sup>2</sup>, Mark Schulz<sup>2</sup>, Ramanand Gollapudi<sup>2</sup>, Sergey Yarmolenko<sup>3</sup>, Sudheer Neralla<sup>3</sup>, Jag Sankar<sup>3</sup>, Yi Tu<sup>4</sup> and Srinivas Subramaniam<sup>1</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, Carpinteria, California.

Highly aligned multi-walled carbon nanotube (MWCNT) 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/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> 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 catalyst performance, the MWCNT arrays were continuously grown for up to 3 hours. Various types of Fe patterning on the Si substrate were tested. MWCNT arrays to 4 mm long were grown by Chemical Vapor Deposition (CVD) from a gas mixture of C<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>-Ar-H<sub>2</sub>O at 750 deg C. Environmental scanning electron microscopy, energy dispersive spectroscopy, and atomic force microscopy were used to characterize the MWCNT morphology. Transmission electron microscopy images of MWCNT arrays show that the nanotubes typically have a 20 nm outer diameter and 8 nm inner diameter. Based on these results, the top growth mechanism was verified and the reason for the MWCNT growth stopping was investigated. To investigate applications, nanotube towers 1 mm x 1 mm x 4 mm in size were grown and easily peeled off the Si wafer. Each tower contains about 1 billion individual nanotubes with 20-30 nm diameters. Electrochemical actuation of one MWCNT tower was demonstrated in a 2M NaCl solution. MWCNT 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 in the axial direction compared to previous entangled 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 mM K<sub>3</sub>(CN)<sub>6</sub> ferrocyanide solution. The CV response showed ideal characteristics for biosensor development. The as-grown (no purification or functionalization) nanotube tower was cast in epoxy and the elastic modulus was evaluated using nanoindentation. The Youngs 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 electrochemical actuation, elastic modulus, and electrical conductivity were much greater than the properties previously obtained by dispersing powdered nanotubes into polymers. The excellent mechanical properties, electrochemical 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.** Yongsoo Shin<sup>1</sup>, Glen E. Fryxell<sup>1</sup>, William D. Samuels<sup>1</sup>, Charles Johnson<sup>2</sup>, Michael M. Haley<sup>2</sup> and Gregory J. Exarhos<sup>1</sup>; <sup>1</sup>Pacific Northwest National Lab, Richland, Washington; <sup>2</sup>Department of Chemistry, University of Oregon, Eugene, Oregon.

Nanoporous carbon scaffolds comprise desirable support materials for catalysis, separation, and sensing applications particularly when the 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 spheres 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 isomeric fructose ring 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) also are prone to analogous condensation 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. For example, mesoporous carbon functionalized with sulfur exhibits a marked adsorption capacity for mercury that is significantly greater than for other cations. The presence of a bound diamine functionality also appears to promote selective organic reactions (Heck coupling) at elevated temperatures. Processing approaches to achieving these chemically modified carbon spheres with interconnected porosity will be described along with attendant behavior with respect to contaminant adsorption and surface reactivity.

#### **O12.22**

**Structural and Spectroscopic Study of the Co Incorporation in to the Lattice of TiO<sub>2</sub>.** Nini Rose Mathews<sup>1</sup>, Erik R. Morales<sup>1</sup>, Joel P. Enriquez<sup>1</sup>, Mari A. Cortes-Jacome<sup>2</sup>, Jose A. Toledo<sup>2</sup>, Concepcion Mejia-Garcia<sup>3</sup>, Gerardo Contreras Puente<sup>3</sup>, Alex Punnoose<sup>4</sup> and Xavier Mathew<sup>1</sup>; <sup>1</sup>CIE-UNAM, Temixco, Morelos, Mexico; <sup>2</sup>Programa de Ingenieria Molecular, Instituto Mexicano del Petroleo, Mexico, Mexico; <sup>3</sup>ESFM, IPN, Mexico, Mexico; <sup>4</sup>Physics, Boise State University, Boise, Idaho.

Development of transition metal doped TiO<sub>2</sub> is interesting due to the possible applications in spintronics, and there are recent reports of the room temperature ferromagnetism in transition metal doped TiO<sub>2</sub>. In this work we are presenting the results of our investigation on the development and characterization of the Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> by XRD, Raman and IR spectroscopic techniques. 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 3 % atomic weight. The XRD analysis showed that the samples are polycrystalline rutile TiO<sub>2</sub> and no other phases could be observed. The grain size showed a dependence on the doping concentration; increases with doping and attained a maximum 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 TiO<sub>2</sub>, and additional bands are observed in doped samples indicating incorporation of Co into the lattice.

#### **O12.23**

**Growth of Metal Nanoparticles on Single-Wall Carbon Nanotubes and Nanohorns.** Hongtao Cui<sup>1</sup>, David B. Geohegan<sup>1</sup>, Alex A. Puzosky<sup>1</sup>, Iliia N. Ivanov<sup>1</sup>, Andrew Lupini<sup>1</sup>, Stephen J. Pennycook<sup>1</sup>, Jianxin Zhong<sup>2</sup> and G. Malcolm Stocks<sup>3</sup>; <sup>1</sup>Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>2</sup>Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; <sup>3</sup>Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Carbon nanotubes represent an important class of one-dimensional materials that can be used as supports for metal nanoparticles for application in hydrogen storage, catalysis, biology, and photovoltaics. A unique structural feature of carbon nanotubes is their well-defined and unusually large surface curvatures. However the mechanisms governing the size and stability of nanoparticles grown onto these curved surfaces of nanostructures is largely unexplored. From the continuum theory of elasticity, it is expected that metal nanoparticles would undergo bending deformations as they interact with such nanoscale curved surfaces; a continuous film can therefore not coat the nanotubes. We have explored the size and stability of metal nanoparticles grown by electron beam evaporation onto the sidewalls of purified single-wall carbon nanotubes obtained by laser vaporization growth and deposited onto TEM grids. Transition-metal nanoparticles including platinum, gold, silver, and titanium were processed at various conditions. The influence of these parameters (including temperature) on the nanoparticle morphology and aggregation were observed using high resolution phase-contrast and Z-contrast transmission electron microscopes. This research was supported by the Laboratory-Directed Research and Development Fund at Oak Ridge National Laboratory and the Department of Energy Center of

Excellence on Carbon-based Hydrogen Storage Materials.

#### **O12.24**

**Carbon Nanotube Arrays as Filters and Collector Elements in High-Performance Liquid Chromatography (HPLC) Systems.** Brian Dick, Aleksandr Noy and Olga Bakajin; Lawrence Livermore Nat'l Lab, Livermore, California.

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. Multiwall 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 microfabrication 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 within etched silicon channels. We have demonstrated that channels (typical cross sectional dimensions of 250um in width by 20 to 50um in height) can be easily filled by the MWCNT monolithic structure with length scales of 100um to 10cms. The pore size and separation within these arrays are 50nm. The filter 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 spectrographic analysis at the channel outlet.

#### **O12.25**

**Spin-Spin Interactions in Cu<sup>2+</sup> Exchanged Faujasite-X Zeolite.** Chrispin B. O. Kowenje, Barry Jones and David C.

Doetschman; Chemistry, SUNY, Binghamton University, Binghamton, New York.

The interpretation of the EPR spectra of Cu<sup>2+</sup> exchanged Faujasite zeolite is not straightforward. Recent literature points to the role of both the Cu<sup>2+</sup> zeolite sites and the Cu<sup>2+</sup> relationship to lattice Al in determining the parameters of Cu<sup>2+</sup> spin Hamiltonian. Our work showed that at low concentration (< 8 Cu per unit cell of zeolite), the Cu<sup>2+</sup> EPR signals show negligible spin-spin interactions. The relative intensities of the two Cu<sup>2+</sup> spectra observed at low Cu<sup>2+</sup> exchange is determined by the probabilities of Al distribution in the six-ring of site II. Above 8 Cu per unit cell, both the CW EPR and the spin relaxation parameters of Cu<sup>2+</sup> 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.** Turgay Kacar<sup>1,2</sup>, Melvin Zin<sup>3</sup>, Alex Jen<sup>2</sup>, Candan Tamerler<sup>1,2</sup> and Mehmet Sarikaya<sup>2,1</sup>; <sup>1</sup>Molecular Biology and Genetics, Istanbul Technical University, Maslak - Istanbul, Turkey; <sup>2</sup>Materials Science and Engineering, University of Washington, Seattle, Washington; <sup>3</sup>Chemical Engineering, University of Washington, Seattle, Washington.

We demonstrate design and engineering of a gold-binding protein genetically fused to alkaline phosphatase and present a procedure of the fabricated assembly of the construct with retained inorganic-binding and enzymatic bi-functional activity. The gold binding protein (GBP-1) is a 14-amino acid polypeptide, MHGKTQATSGTIQS that was combinatorially selected using cell surface display using maltoporin, LamB, 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 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 biosorption and measured the catalytic activity of the AlkP spectrophotometrically by monitoring phenol formation from the reaction with pyronitrophenyl phosphate. The enzymatic activity was absent when wild-type AlkP alone (without the fused GBP-1) which probably physisorbed on gold. We fabricated micropatterned gold surfaces by using thiol-anchored polyethylene glycol that was stamped using soft lithography and, thus, creating addressable hydrophilic/hydrophobic regions on the surfaces. Using the micropatterned substrates we directed-assembled GBP-1/AlkP constructs within 5-mm diameter hydrophobic regions and demonstrated its retained enzymatic activity. The protocols developed can be of great utility for spatially distributed biosensing and bioreactivity for single or more functions. This work is supported

by TR-SPO, US-ARO-DURINT and AFOSR Bioinspired Systems Programs.

#### **Q12.27**

##### **Temperature Dependence of the Electronic Transition Energies in Individual Carbon Nanotubes.**

**Stephen Cronin**<sup>1</sup>, Yan Yin<sup>3</sup>, Andrew Walsh<sup>3</sup>, Rodrigo Capaz<sup>4,2</sup>, Alexander Stolyarov<sup>5</sup>, Paul Tangney<sup>2</sup>, Marvin Cohen<sup>2</sup>, Steven Louie<sup>2</sup>, Anna Swan<sup>3</sup>, Selim Unlu<sup>3</sup>, Bennett Goldberg<sup>3</sup> and Michael Tinkham<sup>5</sup>; <sup>1</sup>University of Southern California, Los Angeles, California; <sup>2</sup>University of California, Berkeley, California; <sup>3</sup>Boston University, Boston, Massachusetts; <sup>4</sup>Universidade Federal do Rio de Janeiro, Caixa, Rio de Janeiro, Brazil; <sup>5</sup>Harvard University, Cambridge, Massachusetts.

Tunable Raman spectroscopy is used to measure the optical transition energies  $E_{ii}$  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 suspended over trenches we eliminate the effects of interaction with the substrate, surfactant molecules and other nanotubes. For all nanotubes measured  $E_{ii}$  is observed to shift down in energy by as much as 50meV, from -160 to 300°C, in contrast to previous measurements performed on nanotubes in alternate environments, which show upshifts and downshifts in  $E_{ii}$  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.

#### **Q12.28**

##### **In-situ Protein Detection Using a Piezoelectric Microcantilever Sensor.**

**Joseph Capobianco**, 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 their position to lower frequencies 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 laser monitoring required in 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 PMNPT-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 (methyltrimethoxysilane) was sufficient to prevent the PZT-glass system from shorting in PBS (phosphate buffered saline) for a time periods in excess of two hours. Similarly, it has been shown that a coating of parylene-c can successfully insulate the PMNPT-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  $\alpha$ EGFR. 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. Adams of Fox Chase Cancer Center is used for the HER-2 and  $\alpha$ EGFR. 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 metal-chelate technique can be used to immobilize the scFv to the surface through a HIS-tag(6x). 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.

#### **Q12.29**

##### **The effect of the size of gold nanoparticles on the catalytic activity of oxidative decomposition reaction of CH<sub>3</sub>CHO.**

**Koji Tajiri**, Yutaka Tai, Shihō Nagano and Jeong-Kwon Lee; AIST, Nagoya, Japan.

The composites that 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 at 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 ripened under carefully controlled temperature and period 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 nanoparticles 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 fairly 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.

#### **Q12.30**

##### **Stable and Reproducible Chain-like Assembly of Gold Nanoparticles for Surface-enhanced Raman Scattering.**

**Takao Fukuoka**<sup>1</sup>, Ryosuke Kuramoto<sup>2</sup>, Nagisa Shinohara<sup>2</sup>, Shuzo Ikuta<sup>2</sup>, Motofumi Suzuki<sup>3</sup> and Yasushige Mori<sup>2</sup>; <sup>1</sup>JST Kyoto CREATE, Seika chō, Kyoto, Japan; <sup>2</sup>Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Japan; <sup>3</sup>Department 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). Longitudinal LPR of the gold nanoparticles connected in chain 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 hydrosol 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 1s to 30s) 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 s 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 were observed. These wavelength of LPR of assemblies were theoretically discussed. Prepared SERS substrate was the hydrosol 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 retained more than three months although it was fluid hydrosol. Aggregation size L and numbers of particles N in the aggregation were also counted from the TEM images. Fractal dimension  $df (= \log N / \log L)$  increased from 1.2 to 1.8 according with the growth of the aggregation. These facts indicate that we can observe snap shot of the propagation of chain-like growth by diffusion limited aggregation of the gold nanoparticle.

#### **Q12.31**

##### **Functionalized Nanocomposite Silica Thin Films for Sensing Applications.**

**Andrew M. Dattelbaum**<sup>1</sup>, Gary A. Baker<sup>1</sup>, Hsing-Lin Wang<sup>1</sup>, Atul N. Parikh<sup>2</sup> and Andrew P. Shreve<sup>1</sup>; <sup>1</sup>Bioscience Division, Los Alamos National Lab, Los Alamos, New Mexico; <sup>2</sup>Applied Science, University of California, Davis, California.

The preparation and characterization of functional nanocomposite silica thin film mesophases for sensing applications will be described. Incorporation of fluorescent molecules or polymers into mesostructured silica thin films has attracted attention for use as optically active materials. Thin film silica mesophases functionalized with luminescent species were prepared by an evaporation-induced self-assembly process involving hierarchical organization of organic surfactant and inorganic silica building blocks. Optically active, luminescent molecules or polymers have been encapsulated within these films to prepare films responsive to changes in pH, O<sub>2</sub> or nitroaromatic vapor-phase molecules. For films sensitive to nitroaromatic vapors, we show that by changing the properties of the surfactants used to template the mesostructure of the nanocomposite film, we can control the doping concentration and luminescence properties of the functionalized films. In addition, exposure of selected films to deep-UV light is shown to be effective at preparing patterned, optically active nanocomposite thin films.

### **O12.32**

**Controlled Growth of Gold Nanorod Arrays from Polyethyleneimine-coated Alumina Templates.** Jeong-Mi Moon and Alexander Wei; Chemistry, Purdue University, West Lafayette, Indiana.

Au 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 controlled. The local length distribution was extremely narrow 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 grains 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.

### **O12.33**

**Surface Stress Effects on the Elastic Behavior of Nanoporous Metals.** D. A. Crowson, D. Farkas and S. G. Corcoran; Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Nanoporous metals formed by the electrochemical process of de-alloying possess a bi-continuous metal-void 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 electrodes for sensor/actuator applications. Surface stress related effects, as well as surface relaxations, become very important as a result of the size scale of these structures. We present a method for generating digital samples that are representative of the real structures formed by de-alloying. 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 important effects of surface relaxations on the elastic behavior of these materials.

### **O12.34**

**Synthesis of Nanoporous GaN Crystalline Particles by Chemical Vapor Deposition.** Joan Carvajal, 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 catalysis. 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 magnetism, catalysis, and biotechnology. 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 methods, 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. Synthetic 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 NH<sub>3</sub>, nanoporous GaN particles with a pore size 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 micron-size particles reveals a regular array of nanopores closely aligned along the [0001] 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.

### **O12.35**

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

The biological macro-molecule Ferritin (an iron-storage protein) has long been recognised as a useful template within which to synthesise size-constrained, functional nano-particles. The outer protein shell (diameter 12nm) confers on the overall particle: size mono-dispersity; 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); CdSe (optical/electro-luminescence). We are particularly interested in magnetite-cored ferritin (so-called Magneto-Ferritin), 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 separated product (by chemical assay, 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.

### **O12.36**

**Characterization of Individual Zinc Oxide Nano-Belts and Nano-Rings by using X-Ray Nano-Diffraction Technique.** Iuliana Cernatescu<sup>1</sup>, Yanan Xiao<sup>2</sup>, Zhonghou Cai<sup>2</sup>, Puxian Gao<sup>1</sup>, Zhong Lin Wang<sup>1</sup> and Robert L. Snyder<sup>1</sup>; <sup>1</sup>Materials Science & Engineering, Georgia Institute of Technology, Atlanta, Georgia; <sup>2</sup>Experimental Facilities Division, Argonne National Laboratory, Argonne, Illinois.

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 future 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 characterization of 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 SEM/TEM. [1] Zhao M. H., Wang Z.L., Mao S. X., Nano Letters, 2004, 4, 587. [2] Xiao, Y.; Cai, Z.; Wang, Z. L.; Lai, B.; Chu, Y. S. J. Synchr. Rad., 2005, 12(2), 124.

### **O12.37**

**Integration of indium oxide nanowire sensors with low-power microheaters.** Daihua Zhang, Kounghmin Ryu, Xiaolei Liu, Chao Li, Bo Lei and Chongwu Zhou; Electrical Engineering, University of Southern California, Los Angeles, California.

We have assembled indium oxide nanowires with low-power microheaters 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 is highly sensitive to a wide variety of chem/bio species including oxygen, ethanol, carbon monoxide, nitrogen dioxide and dimethylmethylphosphonate, 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 molecular adsorbate 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 Batteas<sup>1</sup>, Charles M. Drain<sup>2</sup>, Chang Xu<sup>3</sup> and Kate Beers<sup>3</sup>; <sup>1</sup>Department of Chemistry, Texas A&M University, College Station, Texas; <sup>2</sup>Department of Chemistry and Biochemistry, Hunter College/CUNY, New York, New York; <sup>3</sup>NIST, Gaithersburg, Maryland.

Surface energies have been found to be effective in controlling the surface assembly morphology in organic nanoparticles. Here, nanoparticles of an Fe(III) porphyrin appended with four N-polyethyleneglycopyridinium moieties prepared in acetonitrile were deposited onto hydrophilic 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 thick 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/acetonitrile solvent and the surface. Mechanisms for the control of nanoparticle morphologies by varying surface energies are discussed, and aspects of this work are generally applicable to 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 onto a silicon oxide surface based on waveguide mode.** Nobuko Fukuda<sup>1</sup>, Makoto Fujimaki<sup>1</sup>, Koichi Awazu<sup>1</sup>, Kaoru Tamada<sup>2</sup> and Kiyoshi Yase<sup>1</sup>; <sup>1</sup>AIST, Tsukuba, Japan; <sup>2</sup>TIT, 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 a polarized He-Ne laser. When 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 protein probe. 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-patterning 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 TiO<sub>2</sub> Thin Films By CM-GFS Source.** Kazuya Oguri<sup>1</sup>, Mitsuo Iwase<sup>1</sup>, Hiroyuki Nishino<sup>1</sup>, Masahiro Yamazaki<sup>1</sup> and Susumu Masaki<sup>2</sup>; <sup>1</sup>Dep. of MS, Tokai Univ, Hiratsuka, Japan; <sup>2</sup>Tokyo National College of Technology, Tokyo, Japan.

We produced original sputter device CM-GFS source. Pt doped TiO<sub>2</sub> thin films were deposited by CM-GFS source. The thin film that had deposited by this device was evaluated. When sputtering the Ti only, TiO<sub>2</sub> thin films are formed in anatase structure and co-sputtering Ti and Pt, The TiO<sub>2</sub> thin films are formed in rutile structure. 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 microscope (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/TiO<sub>2</sub> that deposited by CM-GFS showed the photo catalyst. It was possible to apply with the gas sensor.

### O12.41

**Dramatic Stabilization of Proteins Through Control of Their Nanoscale Environment.** Prashanth Asuri, Sandeep S. Karajanagi, Ravi S. Kane and Jonathan S. Dordick; Chemical and Biological Engineering, Rensselaer Polytechnic Institute, Troy, New York.

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 macroscopic supports. Various enzymes adsorbed onto SWNTs were more active and stable at high temperatures and in organic solvents as compared to conventional macro/microscale supports such as graphite. The enhanced stability of the enzymes adsorbed onto the nanoscale materials 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 as 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 Titanate-Based Nanotubes and Nanoribbons.** Denis Arcon<sup>1,2</sup>, Polona Umek<sup>1</sup>, Pavel Cevc<sup>1</sup>, Alexandre Gloter<sup>3</sup> and Christopher Ewels<sup>3</sup>; <sup>1</sup>Solid State Physics Department, Institute Jozef Stefan, Ljubljana, Slovenia; <sup>2</sup>Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia; <sup>3</sup>Laboratoire de Physique des Solides, Université Paris-Sud, Orsay, France.

The intensive study of catalytic reactions of NO<sub>x</sub> 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 NO<sub>x</sub> 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)<sub>2</sub>Ti<sub>n</sub>O<sub>2n+1</sub> materials where the basic framework consists of TiO<sub>6</sub> octahedra arranged in planes. Na or H ions take interlayer positions and surfaces may be passivated by hydroxyl groups. Samples were exposed to a NO<sub>2</sub> atmosphere in order to test their adsorption properties using pulsed EPR. The nanotubes were found to have high active surface areas of about 250 m<sup>2</sup>/g. When exposed to NO<sub>2</sub> gas, NO<sub>2</sub> molecules tend to physisorb on the nanotube surface via the nonbonding p<sub>y</sub> orbital of the oxygen atoms. In contrast nanoribbons have much smaller active surface areas (~30 m<sup>2</sup>/g). The dominant EPR signal now comes from NO molecules adsorbed on Na<sup>+</sup> ions. We propose that on a hydrolysed surface of nanoribbons, NO<sub>2</sub> bind in pairs, resulting finally in NO<sub>3</sub> and NO with some released water. NO<sub>3</sub> is EPR silent and we thus cannot observe it in our experiments. On the other hand we clearly observe NO in abundance in nanoribbons and to a much lesser degree in nanotubes. If Na<sup>+</sup> ions can catalyse this reaction, this would explain the higher concentration of NO seen in the nanoribbons where the Na concentration is higher. Nanotubes also have hydrolysed 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 NO<sub>2</sub> 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 NO<sub>2</sub> molecules on the titania-based surface. Our results show that titania nanotubes and nanoribbons can serve as adsorbents and even as catalysis material for NO<sub>x</sub> removal. They thus have strong and nearly immediate application potential.

### 8:30 AM \*O13.2

**Supported Gold Nanoparticles for the Oxidation and Sensing of CO and Hydrogen.** Masatake Haruta, Faculty of Urban Environmental Sciences, Materials Chemistry Course, Tokyo



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 273K and the direct gas phase epoxidation of propylene with oxygen and hydrogen. The role of nanostructure in the genesis of unique catalytic properties of Au nanoparticles is discussed for low-temperature CO oxidation. The strong contact of Au particles with 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 on the support sides but close to the perimeter. Hemispherical Au particles attached to the support at their flat planes provide longer perimeter distance. Selection of support metal oxides does not affect the catalytic activity for H<sub>2</sub> oxidation but dramatically changes that for CO oxidation. It is advantageous in 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)<sub>2</sub> support, only small Au clusters composed of 13 atoms clusters with icosahedral structure are active. Gold nanoparticles combined with 3d transition metal oxides can detect CO and H<sub>2</sub> by the change in the optical absorbance in the wavelength range of 400 to 900nm. It is also possible to recognize CO from H<sub>2</sub> by monitoring absorbance changes at two different wavelengths, for instance, at 600nm caused by plasmon absorption over Au surfaces and at 900nm caused by the change in positive hole density of semiconductive metal oxide supports. References 1) M. Haruta, Chem. Record **3**, 75-87(2003). 2) M. Date, M. Okumura, S. Tsubota and M. Haruta, Angewandte Chem. Intern. Ed. **43**, 1546-1548(2004). 3) M. Ando, T. Kobayashi, S. Iijima and M. Haruta, J. Mater. Chem. **7**, 1779-1783(1997).

#### 9:00 AM O13.3

##### Emergent Nanostructures in Conducting Polymers.

Sanjeev K. Manohar, Xinyu Zhang 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, polythiophene, 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 nanofibrillar conducting polymers are synthesized directly in their electronically conducting doped form, e.g., the 4-probe pressed pellet conductivity values obtained are: polyaniline.HCl (5 S/cm), polypyrrole.Cl (30 S/cm), PEDOT.Cl (15 S/cm) and polythiophene.Cl (20 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 peroxydisulfate oxidant proceeds via the intermediacy 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 size aggregates during the induction period just prior to the onset of polymerization. We believe these aggregates are composed of clusters of anilinium cation and peroxydisulfate 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 seed aggregates forming in situ during the early stages of the reaction. The intermediacy 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 qualitative parallels between organic precipitation polymerization reactions and inorganic biomineralization processes.

#### 9:15 AM O13.4

##### 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 biochemistry 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 traditional biological techniques, (PAGE gels, 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. Nano-surface 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 O13.5

##### pH Effect on the Optical Properties of Peroxo-Titanium Complex.

Ruxiong Cai<sup>1</sup>, Shun Yung Kwok<sup>1</sup>, Kiminori Itoh<sup>2</sup> and Chang Qing Sun<sup>3</sup>; <sup>1</sup>Singapore Institute of Manufacturing Technology, Singapore, Singapore; <sup>2</sup>Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama, Japan; <sup>3</sup>School 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 H<sub>2</sub>O<sub>2</sub> into freshly prepared, well-washed titanium hydroxide cake, without adding extra acid. A fresh PTC with pH 2.21 exhibits an orange color. However, the pH value rises 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 one year ago. 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 a 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 experiment. 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 245nm for the cloudy yellow samples, being similar to that of colloidal TiO<sub>2</sub>. This suggests that TiO<sub>2</sub> particles might form during the increase in pH value. This is supported by the fact that TiO<sub>2</sub> particles were observed under TEM for a sample with pH 8.37. The formation of TiO<sub>2</sub> particles accelerated from pH 5.8 and above, but not in acidic conditions. In an H<sub>2</sub>SO<sub>4</sub> acidified environment, the PTC color turned red-orange and a new absorption peak developed at 397nm 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 [O<sub>2</sub>Ti(SO<sub>4</sub>)]<sup>2-</sup>. In this study, we clearly demonstrated that the orange color of PTC was produced in the absence of H<sub>2</sub>SO<sub>4</sub>, suggesting that the [O<sub>2</sub>Ti(SO<sub>4</sub>)]<sup>2-</sup> model is not reasonable. Based on the results, we can say that the UV spectrum was influenced by adding extra acid (H<sub>2</sub>SO<sub>4</sub>). The traditional quantitative measurement based on the absorption at 410 nm is likely to occur with H<sub>2</sub>SO<sub>4</sub>-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 O13.6

**Synthesis and Characterization of Tailored Magnetic Ceramic Nanoparticles: Iron Oxide, Cobalt Oxide, and Manganese Oxide.** Bernadette A. Hernandez-Sanchez<sup>1</sup>, Timothy N. Lambert<sup>2</sup>, Harry D. Pratt<sup>1</sup>, Nelson S. Bell<sup>2</sup>, Blake A. Simmons<sup>3</sup>, Francois Leonard<sup>3</sup>, Thomas J. Headly<sup>2</sup> and Timothy J. Boyle<sup>1</sup>; <sup>1</sup>Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, New Mexico; <sup>2</sup>Chemical Synthesis & Nanomaterials, Sandia National Laboratories, Albuquerque, New Mexico; <sup>3</sup>Nanoscale Science & Technology, Sandia National Laboratories, Livermore, California.

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 CdE (E = S, Se, Te) or ZnO with Au or magnetic tips. This structure 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, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, CoO, and MnO. These metal oxides nanoparticles were synthesized from their respective mesityl precursors [Fe(Mesityl)<sub>2</sub>]<sub>2</sub>, [Mn(Mesityl)<sub>2</sub>]<sub>3</sub>, and [Co(Mesityl)<sub>2</sub>]<sub>2</sub> (where mesityl = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) using 1-octadecene (320 °C) and trioctylamine (365 °C) as the solvents. The particles were characterized using powder X-ray diffraction, TEM, energy dispersive spectroscopy, and SQUID as spherical (5–15 nm) and square (~20 nm) crystalline nanoceramic materials. In order to make these nanoceramic materials more useful, 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, these probes also have the potential to be used as biological sensor 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-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

#### 10:30 AM O13.7

**A New Strategy for Synthesis of Bimetallic Nanoparticles.** Peter N. Njoki, Jin Luo, Aisley Jacob, Rizwan Munawar and Chuan-Jian Zhong; Chemistry, State Univ. of New York at Binghamton, Binghamton, New York.

The ability to control composition and size in the synthesis of bimetallic nanoparticles is important for the exploitation of the bimetallic catalytic properties. 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 via reduction of AuCl<sub>4</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> using a combination of reducing and capping agents. Mechanistically, the reduction of Au(III) was catalyzed by the formation of Pt as a result of the reduction of Pt(II). By controlling the feed ratios of AuCl<sub>4</sub><sup>-</sup> and PtCl<sub>4</sub><sup>2-</sup> and the relative concentrations, an effective route for the preparation of AuPt nanoparticles with bimetallic compositions ranging from ~ 0-90 Au% and particle sizes ranging from 2 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 O13.8

**Fabrication and Characterization of Solution-Phase, Triangular Ag Nanotriangles with Controllable Size.** Jing Zhao<sup>1</sup>, Amanda J. Haes<sup>2</sup>, Xiaoyu Zhang<sup>1</sup>, Erin M. Hicks<sup>1</sup>, George C. Schatz<sup>1</sup> and Richard R. Van Duyne<sup>1</sup>; <sup>1</sup>Chemistry, Northwestern University, Evanston, Illinois; <sup>2</sup>Naval Research Laboratory, Washington DC, District of Columbia.

A novel method to produce solution-phase triangular silver nanoparticles is presented. Ag nanoparticles are prepared by nanosphere lithography and are subsequently released into solution. The resulting nanoparticles are asymmetrically functionalized to produce either single isolated nanoparticles or dimer pairs. The structural and optical properties of Ag nanoparticles have been characterized. Mie theory and the Discrete Dipole Approximation

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

#### 11:00 AM O13.9

**Nanowire-based Gas-Sensors: Synthesis and Device Application.** Sanjay Mathur, Sven Barth, Hao Shen and Thomas Ruegamer; 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 crystalline 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-tert.butoxide on silicon and alumina substrates. 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 SnO<sub>2</sub> 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 nanowires of different diameters were used to construct miniaturized optical switches, which could be addressed 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.

#### 11:15 AM O13.10

**Direct formation of highly porous gas-sensing films by *in-situ* thermophoretic deposition of flame-made Pt/SnO<sub>2</sub> nanoparticles.** Lutz Madler<sup>1</sup>, Albert Roessler<sup>1</sup>, Sotiris E. Pratsinis<sup>1</sup>, Thorsten Sahn<sup>2</sup>, Alexander Gurlo<sup>2</sup>, Nicolae Barsan<sup>2</sup> and Udo Weimar<sup>2</sup>; <sup>1</sup>Department for Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland; <sup>2</sup>Institute 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 9 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 SnO<sub>2</sub> 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), 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.