

SYMPOSIUM R

Nanoporous and Nanostructured Materials for Catalysis, Sensor, and Gas Separation Applications

March 28 - April 1, 2005

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* Invited paper

SESSION R1: Porous Nanostructures by Anodic Oxidation

Chair: Horst Hahn

Monday Afternoon, March 28, 2005
Room 3001 (Moscone West)

1:30 PM *R1.1

Ordered Porous Alumina and Related Structures.

Ulrich Goesele, Petra Goering, Woo Lee, Mato Knez, Kornelius Nielsch, Martin Steinhart, Yiming Sun and Danilo Zschech; Max Planck Institute of Microstructure Physics, Halle, Germany.

The present state-of-the-art fabrication of ordered porous alumina will be described, including first attempts to either decrease the pore radius by atomic layer deposition or by incorporating pore forming materials with smaller pore diameters in the original pores. Nano-imprint approaches for long-range ordered pore arrays will be discussed. Formation of versatile gold membranes based on porous alumina and their properties and use will be touched upon. A comparison to other materials which may be used to form two-dimensional pore arrays such as macroporous silicon and block-copolymers will be made.

2:00 PM R1.2

Nano-porous Titanium Oxide Morphologies Produced by Anodizing of Titanium. Glenn Paul Sklar, Harpreet Singh, Vishal Mahajan, Devendra Gorhe, Shantanu Namjoshi and Jeff C. LaCombe; Materials Science, University of Nevada, Reno, Reno, Nevada.

A quick and dependable technique has been worked out to produce a variety of nano-porous titanium oxide surfaces on titanium metal. The process employs mild chemical conditions and ambient temperature. Other researchers have produced similar results by titanium anodizing (1-3). Our method is faster, more controllable, and covers the entire metal surface every time. These morphologies may have use in adhesive bonding, dye-sensitized solar cells, gas sensing membranes, and other electrode systems. (1) D. Gong, et al., J. Materials Research 16, 3331 (2001). (2) V. Zwilling, et al., Electrochimica Acta 45, 921 (1999). (3) R. Beranek, et al., Electrochemical and Solid-State Letters 6, No. 3, B12 (2003).

2:15 PM R1.3

The Synthesis of Alumina Nano-Fibers, Grown on the Surface of a Porous Alumina Membrane. Ryan S. McGrath, MS&E, University of Nevada, Reno, Nevada.

It has been shown that self-ordering nanoporous alumina can have beneficial properties in forming filtration membranes [1]. The goal of this study was to create a permeable alumina membrane with a very high surface area and large pore diameter for filtration purposes. Phosphoric acid as an electrolyte provides the self-ordering formation of relatively large pores (300nm diameter) compared to other more commonly studied electrolytes as sulfuric or oxalic acids. The concern with Phosphoric acid is that the high voltages used result in a sensitive balance of anodizing conditions to achieve a well ordered structure without etching. The common solution is to do anodizing at 0-3°C [2], hence slowing down the reaction rate. This study sought to find more mild conditions at room temperature that still provide an ordered structure. To further increase the surface area of the membrane we can adjust the anodizing conditions to start growing alumina fibers that originate on the surface of the alumina membrane at the edges of the hexagonal inter-pore structure. The fibers tangle together as they grow longer; eventually creating a tangled mesh layer above the porous layer. SEM photographs show fibers that are approximately 2µm long and ranging in diameter from 1 to 50nm. The aluminum sub matrix can be chemically removed and the alumina barrier layer dissolved to leave a porous alumina membrane with very high surface area alumina fibers on one face. Some possible future applications of this high surface area structure involve filtration of liquids and gasses, chemical deposition of catalyst on the surface area, and heat exchange membranes to name a few. [1] W.R. Rigby, et al., Trans. Inst. Metal Finish. 1990, 68 (3), 95. [2] A. P. Li, et al., J. o App. Physics, 84 (11), 1998.

2:30 PM R1.4

Fabrication of Patterned Arrays with Alternating Regions of Aluminum and Porous Aluminum Oxide. Dmitri A. Brevnov¹, Marcos J. Barela¹, Todd M. Bauer², Gabriel P. Lopez¹ and Plamen B. Atanassov¹; ¹Chem & Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; ²Sandia National Laboratories, Albuquerque, New Mexico.

Anodic aluminum oxide (AAO) arrays are self-ordered porous structures, which are suitable for many technical applications. These arrays exhibit the hexagonal pore arrangement, a very high aspect ratio of 1000 (pore length to pore diameter) and a high pore density. Although AAO arrays have been demonstrated to provide the basis

for the fabrication of nanostructures, the commercial applications of this material have been limited due to the low mechanical strength of aluminum oxide and the difficulty in integrating this material into micro-fabricated devices. In this presentation, a procedure is described for the fabrication of patterned AAO arrays by using a dense barrier aluminum oxide layer as the anodization mask. This fabrication procedure includes the following steps. The aluminum film is patterned with a photoresist and then briefly anodized at a high voltage. The high voltage produces a thin, dense layer of barrier aluminum oxide. The photoresist is then removed and the aluminum film is again anodized at a low voltage to grow porous aluminum oxide. The dense barrier aluminum oxide acts as an anodization barrier thus leaving the underlying aluminum intact. Using this procedure, we are able to fabricate AAO arrays on silicon wafers, which consist of alternating regions of porous aluminum oxide and aluminum metal perpendicular to the silicon substrate. The examination of micrographs suggests that there is a pore curvature at the aluminum/ porous aluminum oxide interface. This curvature is most likely due to both the volumetric expansion during anodization of aluminum to aluminum oxide and lowering of the porous oxide growth rate in the proximity of the barrier aluminum oxide mask. In contrast to previously reported methods, this procedure is more economical, involves fewer steps and is compatible with conventional micro-fabrication techniques. Nano-structures with alternating regions of aluminum and porous aluminum oxide with a low dielectric constant are attractive for the designs of novel interconnect systems in advanced IC technology. In addition, this structure allows for the integration of AAO into micro-fabricated devices such as pre-concentrators, heat sinks, nanofluidic devices, reinforced membranes for separations and micro-reactors, and gas diffusion electrodes for micro-power sources.

SESSION R2: Novel Concepts and Applications of Nanoporous Materials

Chair: Joerg Weissmueller

Monday Afternoon, March 28, 2005
Room 3001 (Moscone West)

3:00 PM *R2.1

Doubly Bicontinuous Mesoporous Metals. Jonah Erlebacher,

¹Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; ²Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland.

Porous metals are immensely useful for catalysis, sensing, and microfluidics. One material, nanoporous gold (NPG) formed by selective dissolution of silver from gold/silver alloys is a useful material in these contexts in its own right. NPG is a bicontinuous open porous material with ligaments and channels of order 10 nm wide, but whose crystallinity is nonetheless maintained over grains orders of magnitude larger. We discuss here how the utility of NPG may be further expanded when used as a substrate for epitaxial casting of secondary materials. Epitaxial casting refers to epitaxial deposition of a thin film (in this case on a highly curved, topologically complex substrate) followed by dissolution of the substrate. For the case of Pt epitaxially cast on NPG, a doubly bicontinuous microstructure may be formed, with two interpenetrating void spaces separated by a thin, ~1 nm, shell of Pt. Growth kinetics, microstructure, and applications will be discussed.

3:30 PM R2.2

Initial Steps of Surface Restructuring by Dealloying: An

In-situ X-ray Diffraction Study of Cu₃Au(111).

Frank Uwe Renner^{1,2}, Andreas Stierle², Tien Lin Lee¹, Helmut Dosch², Dieter Kolb³ and Jorg Zegenhagen¹; ¹ESRF, Grenoble, France; ²MPI-MF, Stuttgart, Germany; ³Department of Electrochemistry, University of Ulm, Ulm, Germany.

Synchrotron radiation with energies above 10 keV offers the possibility to penetrate relatively thick layers, e.g. coatings, liquid/electrolyte layers or gas environments. X-ray diffraction is therefore a unique *in-situ* tool to study structural changes at surfaces and interfaces of crystalline materials. In the last decade x-ray diffraction was used to study *in-situ* many electrochemical interfaces where the electrical potential provides an additional means of control over the surface dynamics and related atomic surface structures. For the selective electrochemical dissolution of less noble components from (binary) Au alloys it is known that above a critical potential porous Au layers form. Below the critical potential these surfaces are passivated by what is commonly thought to be an atomically smooth Au-rich surface. We present an *in-situ* x-ray diffraction study on the electrochemical selective dissolution of Cu from Cu₃Au(111) surfaces in 0.1M H₂SO₄ electrolyte below the critical potential. On long time scales of the experiment we observe the formation of porous Au layers with a ligament width of about 20nm and an average ligament

distance (pore size) of about 100nm. We could follow the entire structural evolution starting from the formation of a considerably strained ultra-thin (3-monolayer thick) initial Au-rich film at low overvoltages to relatively thicker, unstrained bulk Au films at elevated overvoltages (below the critical potential). The lateral extension of the observed Au islands which are densely covering the surface is not changing during the process but only the thickness. After several hours of experiment at elevated potentials the thickness as determined from the x-ray data reaches the values of the lateral extension, i.e. a porous layer with isotropic average ligament size is formed. The chemical composition of the formed surface structures was determined by performing anomalous diffraction with energies around the Cu K absorption edge. The initial ultra-thin layer showed a Cu content still as high as 40% while for the thicker islands no Cu contribution could be seen. As an additional detail the diffraction data reveals a reversal of the stacking sequence (cba) within the freshly formed fcc surface layers (with respect to the substrate, abc). Depending on the rate of dissolution of Cu this defined stacking can be either maintained in the further growth, or a equal population of both twin domains (abc and cba) can be achieved. After the application of elevated potentials *ex-situ* AFM images were recorded. The images for shorter time scales show a surface densely packed with islands, while at later stages a more open, porous morphology can be observed. All images show a hexagonal arrangement of nearest neighbour islands/ligaments. The imaged island dimensions correspond well to the values determined by the X-ray data.

3:45 PM R2.3

Nanostructured Surfaces for Boiling Enhancement.

Shanghai Li¹, Muhammet Toprak¹, Mamoun Muhammed¹, Richard Furberg² and Bjorn Palm²; ¹Materials Science and Engineering, The Royal Institute of Technology, Stockholm, Sweden; ²Energy Technology, The Royal Institute of Technology, Stockholm, Sweden.

Modification of surfaces and creation of patterned surfaces bearing nanosized features by nanotechnology have been hot issues for scientific and technological research. Porous structures with nanosized features have been investigated for many applications as electrode materials, filtering materials, etc. A potential application of porous metallic materials is in the field of heat pump and refrigeration applications. During the past few decades, a lot of work has been done on the development of enhanced nucleate boiling surfaces. The porous metallic coating is considered to be the most viable enhancement technique. The coated layer can be fabricated by various techniques, such as sintering, spraying, painting, electroplating, etc. Studies have shown that most microstructures are effective in reducing the wall superheat at boiling incipience and enhancing the nucleate boiling heat transfer and critical heat flux. However, little attention has been paid to the surface modification by nanostructuring to produce high performance nucleate boiling surfaces. Especially a combination of nano-structuring and micro-porous coating is rather promising. Nanoscale inhomogeneities rather than microscopic cavities on the heater surface may have been responsible for the reduced nucleation energy barrier observed at the onset of nucleate boiling. This work reports the fabrication method, which is a modification of the process reported by Shin et al.[1], and the controlling parameters for the formation of nanostructured microporous Cu surfaces, and their performance in boiling applications as enhanced boiling surfaces. These surfaces have been fabricated on Cu plates/stubs by electrodeposition of Cu from a sulphate electrolyte solution, and ramified Cu nanoparticles forming interconnected hollow spheres have been thus obtained. Various processing parameters as the voltage, time, roughness of the substrate, concentration of electrolyte, and their influence on the morphology of the obtained nanostructures have been investigated in order to have a better/higher control on the surfaces and surface features. SEM was used for the evaluation of the surface structures and their morphology. Finally, pool boiling tests have been performed to evaluate the performance of the boiling heat transfer on these surfaces as enhanced surfaces and compared to plain machined roughened flat and highly polished surfaces. As compared to plain machined roughened surfaces, an enhancement of 400% of was achieved. 1. Shin, H. C., Dong, J. & Liu M. Adv. Mater. 15, 1610-1614 (2003)

4:00 PM R2.4

Suppressing Sublimation of Thermoelectric Power Generators using Opacified Aerogel. Jong-Ah Paik, Steven M. Jones, Jean-Pierre Fleurial, Thierry Calliat and Jeffrey S. Sakamoto; Jet Propulsion Laboratory, Pasadena, California.

The recent interest in thermoelectric technology has spurred the development of advanced materials and device technology. In particular, current work at the Jet Propulsion Laboratory has identified aerogel as an effective sublimation barrier for a wide range of thermoelectric technologies based on SiGe, novel Skutterudites, TAGS, PbTe and Bi₂Te₃. Aerogel is typically known as an extremely porous (>99% porous) silicon dioxide, which has very low thermal and

electrical conductivity. Aerogel has interconnected pores, which are generally in the range of angstroms to a few nanometers. As such, the path required for metal vapor to permeate aerogel is extremely tortuous, thus significantly decreasing sublimation rates. Another benefit of using aerogel as a sublimation barrier is that it can also serve as thermal insulation. Since aerogel is made through liquid synthesis it can be cast in or around thermoelectric devices, thus providing intimate contact between the device and the insulation to assist in channeling heat through the thermoelectric legs and eliminate parasitic, lateral heat loss. Opacified silica aerogel exhibits the most promising behavior as thermal insulation and sublimation suppressing coating for thermoelectric power converters. Silica gels were synthesized at JPL using a two-step process, which involved the use of acetonitrile as the primary diluting solvent, which was then extracted under supercritical conditions. Since the operating temperature of skutterudite materials is expected to exceed 700 °C, maintaining aerogel without cracking/shrinking at high temperature is one of primary requirements for the concept to be effective. Silica aerogels and alumina opacified silica aerogel was tested for shrinkage up to 1000 °C in vacuum. Initially, silica aerogel opacified with alumina powder exhibited around 10° linear shrinkage at 1000 °C and stabilized without further shrinkage for more than 200 hrs. Interestingly, the aerogel exhibited different shrinkage/sintering behavior in air versus in vacuum. Moisture in air is believed to be responsible for the increase in shrinkage. Sublimation suppression was studied by two different methods. One involved in-gradient tests, which simulated actual working conditions. In this case, a sample was prepared by surrounding skutterudite legs with aerogel and the sublimation was investigated using post, cross-sectional analysis. The other method was to measure the instantaneous sublimation rate of aerogel-coated coupons. For this experiment, aerogel was cast around a skutterudite coupon and the sublimation rate was measured using thermogravimetric analysis(TGA). The sublimation rate was reduced by a factor of 25 when thermoelectric coupons were encapsulated with opacified silica aerogel compared to uncoated samples. Details involving the relationship between sublimation suppression rates and the density of aerogel and the effects of thermal conductivity on sublimation suppression will also be presented.

4:15 PM *R2.5

Reversible Strain in Porous Metals Charged in Electrolytes.

Dominik Kramer, Institute of Nanotechnology INT, Forschungszentrum Karlsruhe GmbH, Karlsruhe, Germany.

Because of the high surface-to-volume ratio of nanomaterials, changes at the surface can contribute significantly to the materials overall properties. In the case of an electrode, the surface charge density can be readily varied by applying a bias voltage relative to a counter electrode in the same electrolyte. Therefore, it has been suggested that it should be possible to tune electron-density dependent structural and physical properties of conducting nanomaterials with their high surface-to-volume-ratio using an external voltage [1]. One example of such tuneable properties are the lattice constant and the dimensions of porous samples with nanosized metal structures, which vary in response to changes in the surface stress of the porous bodies. The results shown here are an experimental evidence that the strain in a metal can indeed be reversibly changed by charging the nanoporous sample in an electrolyte. We present in-situ dilatometer and X-ray measurements of two different kind of materials: nanocrystalline metals obtained by compacting nanocrystalline powders on the one hand and nanoporous metals obtained by dealloying on the other hand. Nanocrystalline platinum samples are an example for the first kind of material [2]. Nanoporous gold and nanoporous gold alloys were obtained by dealloying silver alloys in perchloric acid [3]. In both cases mm-sized samples immersed in various aqueous electrolytes have been investigated. Reversible changes of the length of the samples were observed, dependent on the potential vs. a reference electrode. The maximum strain amplitude is comparable to the that of commercial piezoceramics [2]. In a bimetal foil arrangement consisting of a solid metal layer covered with a layer of nanoporous gold, the strain is converted to a bending movement by simple mechanical amplification. The charge-induced movements of such metal actuators are visible with the naked eye [4], whereas the effects of surface stress could previously only be measured with highly sensitive displacement probes. Our results are of interest for three reasons: First, they prove the concept of tuneable charge-dependent properties of nanomaterials. Second, measurements of the strain of nanoporous metals might be helpful for investigations of the interface stress, which is an important parameter of the interface. Third, they might be useful for actuator applications. They need larger currents than piezoelectric materials, but have the advantage to work with small voltages. [1] H. Gleiter, J. Weissmüller, O. Wollersheim and R. Würschum, Acta Mater. 49 (2000) 737 [2] J. Weissmüller, R.N. Viswanath, D. Kramer, P. Zimmer., R. Würschum, H. Gleiter, Charge-Induced Reversible Strain in a Metal, Science 300 (2003), 312 [3] Erlebacher, J., Aziz, M. J., Karma, A., Dimitrov, N., Sieradzki, K., Nature 410 (2001) 450 [4] D. Kramer, R.N. Viswanath, J.

4:45 PM R2.6

Tuning the Magnetic Moment of Nanoporous Transition Metals by Electrochemical Charging. Christian Lemier¹, Joerg Weissmueller^{1,2}, Sadhan Ghosh¹ and Raghavan Nadar Viswanath¹; ¹Institut fuer Nanotechnologie, Forschungszentrum Karlsruhe GmbH, 76021 Karlsruhe, Germany; ²Fachrichtung Technische Physik, Universitaet des Saarlandes, 66041 Saarbruecken, Germany.

Nanoporous materials exhibit an extreme ratio of surface to volume and, in consequence, surface properties can significantly affect the overall materials behaviour. It has been proposed that changes in the electronic structure in superficial space-charge regions may substantially affect the surface properties and, thereby, the overall materials behaviour [1]. The application of an electric field to a nanoporous material immersed in an electrolyte, gives rise to electric double layer regions at the metal-electrolyte interfaces. The spatial extension of the space-charge region is determined by the Thomas-Fermi screening length, which is in the order of the interatomic spacing for metals. Thus, contrary to the case of semiconductors, the net superficial charge is essentially confined to the surface atomic layer, and the local variation in electron density is comparatively large. In previous experiments it has been shown that by polarizing the surface of metals, changes in the superficial bonding induce stress in the surface layer as well as the bulk, leading to a large reversible change in the lattice parameter of nanoporous Pt [2] and to macroscopically visible bending of nanoporous Au cantilevers [3]. In this contribution, the effect of surface charging on the magnetization is discussed. Since magnetism is strongly related to the electronic density of states, an effect on the magnetic moment can be expected. Changes in the magnetic moment up to 10% have been observed by in-situ charging experiments with thin high surface Ni layers deposited on activated carbon and in inert gas condensed PdNi alloys. Special focus has been on finding the appropriate electrolyte and measurement range to prevent effects due to hydride formation and oxidation. [1] H. Gleiter, J. Weissmueller, O. Wollersheim, R. Wuerschum, *Acta Mater.* 49 (2001), 737. [2] J. Weissmueller, R.N. Viswanath, D. Kramer, P. Zimmer, R. Wuerschum, H. Gleiter, *Science* 300 (2003), 312. [3] D. Kramer, R. N. Viswanath, J. Weissmueller, *Nano Lett.* 4 (2004), 793.

SESSION R3: Capillary Phenomena and Transport

Chair: Jonah Erlebacher
Monday Evening, March 28, 2005
Golden Gate C1/C2/C3 (Marriott)

8:00 PM *R3.1

Solidified Fillings of Nanopores. Klaus Knorr, Technische Physik, Universitaet des Saarlandes, Saarbruecken, Germany.

Molecules ranging in size from He to the n-alkane C19H40 have been embedded and solidified in nanoporous glasses. X-ray-diffraction studies show that the fillings consist of a crystalline component in the pore centres and amorphous bilayer next to the pore walls. The structure of the crystalline component is usually close to that of bulk system, but the melting and other structural transition temperatures are significantly reduced. Anomalous behaviour has been observed e.g. for N2 and the n-alkanes. For N2 the transition into the low-temperature modification is absent in 7nm pores, in medium length alkanes the lamellar ordering of the bulk state is suppressed by the pore confinement. Particular attention will be paid to the melting transition.

8:30 PM R3.2

Cationic Motion and Conduction in Zeolites - A Systematic Study of Anion Effects on Local Motion and Long Range Transport. Hubert Koller¹, Edgar Jordan¹, Dirk Wilmer¹ and Robert G. Bell²; ¹Institute of Physical Chemistry, University of Muenster, Muenster, Germany; ²Davy Faraday Research Laboratory, The Royal Institution, London, United Kingdom.

The ionic motion in zeolites was investigated by solid-state NMR, impedance spectroscopy, quasielastic neutron scattering, and molecular modeling methods. We have initiated this study to explore possible promoting effects by salts included in the zeolite void space towards better ionic conductivity for sensor applications. The idea behind this approach is a strong interaction between cations and zeolite six-ring windows, thus hindering fast ion transport. To this end, a mechanistic study on ionic motion in zeolite is undertaken in order to define dominating effects on ionic mobility and transport. The first study was a computation of energy barriers for sodium cation motion in sodalites using a defect model. Sodium point defects were introduced, and the diffusion barrier between two neighboring six-rings was calculated for different anions in the cage center. The

intracage migration barrier of the anion-free sodalite is clearly reduced, if chloride ions are in the center of the cage: the anion-free system has a barrier of 111 kJ/mol, and the chloride sodalite shows a barrier of 75 kJ/mol. The other halide sodalites studied (Br, I) have similar activation barriers in between (101 kJ/mol). This observation motivated us to investigate further the ionic motion in zeolites with extraframework anions. A dynamic model that is sometimes discussed, when tetraoxoanions are present is the paddle wheel mechanism which stands for a promoting effect of rotating oxoanions on cation transport, based on a dynamic coupling of cations and anions. However, it was not clear, whether such a mechanism exists in zeolites, and therefore we made it to a matter of investigation in our study. Sodalites and cancrinites with different oxoanion fillings (tetrahydroxoborate, sulfate, chromate, carbonate) were prepared. The anion dynamics of tetrahydroxoborate sodalite was studied by quasielastic neutron scattering, and solid state NMR methods. The neutron scattering data indicate anion dynamics with a thermal activation of 13.5 kJ/mol. However, the ionic conductivity at 420 K is below 10⁻⁷ S/cm with an activation barrier of 74 kJ/mol. These activation data do not indicate that a dynamic coupling in the sense of a paddle wheel model exists. Similar observations were made on chromate cancrinite. 17O NMR experiments show that the chromate ions undergo a very fast reorientation, while DC conductivity is thermally activated by 82 kJ/mol. The results indicate that ionic conductivity in zeolites can be increased by cation-anion interactions, but tetraoxoanion reorientations have no promoting effect on long-range cation transport. Two parameters seem to offer a potential for further improvement of DC conductivities: cation site occupancies can be optimized for offering better pathways for cation diffusion, and the cation interaction with six-ring windows in zeolites should be made weaker for still lowering activation barriers. Work is in progress on both effects.

8:45 PM R3.3

The Role of Pore Size, Curvature and Structure on the Thermal Stability of Gold Nanoparticles within Mesoporous Silica. Mangesh T. Bore¹, Hien N. Pham¹, Elise E. Switzer¹, Timothy L. Ward¹, Atsushi Fukuoka² and Abhaya K. Datye¹; ¹Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico; ²Catalysis Research Center, Hokkaido University, Sapporo, Japan.

Metal particles deposited on oxide supports are used extensively as heterogeneous catalysts. It is known that gold nanoparticles show high reactivity for CO oxidation at low temperature, but only when the Au particles are very small (<5 nm). Gold nanoparticles supported on silica show rapid sintering at 200C-400C. It has been suggested that the porosity of the support could play an important role in controlling the sintering of metal particles. But the role of pore size, pore curvature and structure is difficult to study with conventional supported metal catalysts. Surfactant templated mesoporous silica is a promising support material since it provides well defined pores of uniform size and structure. Hence, these silica supports provide ideal model systems for the study of nanoparticle sintering. In this work we prepared highly dispersed gold nanoparticles (<2nm) within the pores of mesoporous silica having pore sizes ranging from 2.2nm to 6.5nm and differing pore structures (2D-hexagonal, 3D-hexagonal, cubic and worm-like). The catalysts were reduced in flowing H2 at 200C and then used for CO oxidation at temperatures ranging from 25C-400C. A combination of high resolution TEM/STEM and SEM was used to measure the particle size distribution and to determine whether the Au particles were located within the pores or had migrated to the external silica surface. We found that in each of the samples, the average particle size exceeded the diameter of the silica pores after high temperature treatment, but pore structure played an important role. In the samples with one dimensional pores we found the majority of Au remained within the pores, despite an increase in size beyond the pore diameter. In contrast, with three dimensional interconnected pores, the Au particles had migrated outside the pores in the silica samples. Pore connectivity is clearly an important factor. We also found that curved pores in aerosol-derived silica were more effective at controlling sintering than the straight pores in MCM-41. There was clear evidence for particle migration (particles migrating outside the pores) as well as Ostwald ripening (particles growing larger than the pore diameter, but still located within the pores). The relative importance of these processes could be controlled by changing the pore size, and pore chemistry (coating the walls with titania). The role of convex versus concave structures could be studied clearly in these samples as well as the importance of pore wall thickness. These results provide insight into how the support pore structure could be engineered to control the processes of thermally induced nanoparticle sintering.

9:00 PM R3.4

Atomistic Simulations of Surface Segregation in Pt-Bimetallic Catalyst Nanoparticles. Guofeng Wang¹, M. A. Van Hove¹, P. N. Ross¹ and M. I. Baskes²; ¹Materials Sciences Division, Lawrence

Berkeley National Laboratory, Berkeley, California; ²MST-8 Structure and Property Relation Group, Los Alamos National Laboratory, Los Alamos, New Mexico.

Pt-bimetallic nanoparticles can be applied as electro-catalysts in lower temperature polymer electrolyte fuel cells. Since Pt is a precious active catalyst with a wide range of applications, it is highly desirable to design catalyst nanoparticles in which the Pt atoms are arranged at their outer surfaces. To this end, we have developed interatomic potentials within the modified embedded atom method (MEAM) for Pt-Ni, Pt-Re, and Pt-Mo alloy systems. Furthermore, we have applied these potentials to investigate the segregation of Pt atoms to the surfaces of their nanoparticles with sizes from 2.5 nm to 5 nm, using the Monte Carlo method. We draw the following conclusions from our simulations at T= 600 K. (1) Due to the surface segregation resulting from a large atomic size difference and a strong ordering tendency of Pt and Ni, the Pt-Ni nanoparticle forms a surface-sandwich structure in which the Pt atoms are strongly enriched in the outermost and third layers while the Ni atoms are enriched in the second layer of nanoparticles. In Pt₇₅Ni₂₅ nanoparticles, a nearly pure Pt outermost surface layer can be achieved. (2) Due to the stronger surface segregation that is caused by the significant surface energy difference between Pt and Re, the equilibrium Pt₇₅Re₂₅ nanoparticles adopt a core-shell structure: a nearly pure Pt shell surrounding a Pt-Re core. (3) In Pt-Mo alloys, the Pt atoms would weakly segregate to the surface. Hence, a mixture of Pt and Mo atoms is found in the surfaces of Pt-Mo nanoparticles. However, the Pt atoms are not distributed uniformly in the outermost atomic layer of Pt-Mo nanoparticles. Instead, the Pt atoms segregate preferentially to the facet sites, less to edge sites, and least to vertex sites.

9:15 PM R3.5

Gas and Liquid Transport through a Carbon Nanotube/Silicon Nitride Permeable Membrane. Jason Holt, Aleksandr Noy, Thomas Huser, David Eaglesham and Olgica Bakajin; Lawrence Livermore National Laboratory, Livermore, California.

A number of recent studies [1-3] have focused on the development of membranes with nanometer-scale pores. Such membranes could find application in the area of size-based chemical and biological separations, provided pore sizes can be reduced to molecular diameters and a high flux of the permeate molecule can be achieved. Carbon nanotubes are an ideal material to serve as a membrane nanopore, given their molecular size and atomic smoothness. We recently developed a technique [4] to use multiwall carbon nanotubes as the pores within a silicon nitride membrane. Tracer studies using organic dyes, CdSe quantum dots, and fluorescently-labeled polystyrene beads have been carried out to estimate the average pore size of such membranes. We observe a strongly size-dependant diffusivity in the 10-15 nm range that cannot be accounted for exclusively by bulk diffusion, suggesting the pore size lies in this range. This agrees with TEM observations of the nanotube inner diameters. These membranes have also been characterized through linear voltammetry in KCl solutions of varying concentration. The membrane conductance is approximately linear in solution concentration down to 10 mM, below which the conductance is insensitive to concentration. This observation is consistent with Debye screening, which occurs when the electrical double layer thickness (Debye length) becomes comparable to that of the pore diameter. Measurements are underway with ions of widely varying sizes (e.g. K⁺, NO₃⁻) to observe the ion exclusion effects expected in this size regime. These membranes have also been characterized in terms of their gas permeability and selectivity. Nitrogen permeability as high as 4.7x10⁻⁴ mole/m²-s-Pa has been measured. Initial studies have not revealed selectivity among the gases surveyed (CH₄, O₂, CO₂, N₂), due to pore sizes more than an order of magnitude greater than the molecular diameters. However, with decreases in membrane pore size (approaching the limit of single wall nanotubes) and chemical functionalization, gas selectivity may be expected.

SESSION R4: Heterogeneous Catalysis based on Nanoporous and Nanostructured Materials
Chair: Song Wei Lu
Tuesday Morning, March 29, 2005
Room 3001 (Moscone West)

8:00 AM *R4.1

Nanostructure Processing of Advanced Catalysts, Sorbents and Separation Media. Jackie Ying, The Institute of Bioengineering and Nanotechnology, The Nanos, Singapore.

Nanostructured materials are of interest for a variety of applications. This talk describes the synthesis and properties of nanocomposite materials for environmental catalysis and toxic gas absorption/remediation. The nanocomposite materials have been

synthesized with ultrahigh surface areas and synergistic effects between components. They were successfully applied as (i) catalysts for the selective catalytic reduction of NO_x by propene in oxygen-rich environment, (ii) catalysts for NO_x storage-reduction, (iii) sorbents for SO₂ storage, and (iv) sorbents for H₂S storage. This presentation also describes the synthesis of novel nanoporous materials by supramolecular templating. These materials were designed with compositional flexibility, as well as tailored pore size, pore structure and particle size. They were successfully applied towards the synthesis and separation of pharmaceuticals.

8:30 AM R4.2

Preparation and Characterization of Fibrous Cerium Oxide Templated from Activated Carbon Fibers. Mark Crocker, Uschi Graham, Rolando Gonzalez, Erin Morris, Gary Jacobs and Rodney Andrews; Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky.

Cerium oxide is employed as a catalyst or catalyst promoter in a number of important chemical processes, including the elimination of pollutants from auto-exhaust gases using three-way catalysts, fluid catalytic cracking in refineries and the dehydrogenation of ethylbenzene to styrene. Ceria also shows promise as a catalyst component for low temperature water-gas shift applications, and the preferential oxidation of CO in hydrogen-rich atmospheres (PROX). In these various applications, the performance of the ceria is strongly dependent on its crystallinity and textural properties, including surface area and porosity. In this context, we are studying the preparation of high surface area cerium oxide using a carbon templating method. Impregnation of a highly mesoporous activated carbon (Darco KB-B) with an aqueous solution of cerium nitrate, followed by carbon burn off, affords ceria with a surface area as high as 148 m²/g. This figure compares favorably with ceria prepared using conventional solution methods (typically 70-125 m²/g). Thermogravimetric studies indicate that ceria formation proceeds via decomposition of cerium nitrate at ca. 473 K; oxidation of the carbon template commences at the same temperature, being facilitated by the release of NO₂ from the Ce compound. Gasification of the template is complete by 773 K. Use of activated carbon fibers (ACFs) as template provides a simple route to fibrous cerium oxide. ACFs were prepared by thermal activation of P-400 Ansham fibers under a flow of steam/N₂ at 1073 K and impregnated as for the Darco activated carbon. The lower surface areas (~3 - 40 m²/g) of the resulting ceria products reflect the largely microporous nature of the ACFs; the Ce nitrate solution is evidently unable to penetrate their micropores. Consequently, the surface area of the ceria product is found to increase with increasing mesoporosity of the ACF template. Electron microscopy reveals that the ceria fibers are composed of highly crystalline primary particles, of 5-10 nm diameter; further, the fibers display a number of interesting morphological features at the macro- and nano-scales. For ACF-templated ceria, fiber formation appears to proceed via crystallite growth on the outer surface of the ACF, followed by ACF gasification. In contrast, for Darco-templated ceria aggregates with undefined morphology are obtained, derived from crystallite growth in the template pores.

8:45 AM R4.3

Size and Shape Dependent Catalytic Properties of Pt Nanoparticles Supported on Mesoporous SBA-15 Silica. Robert M. Rioux^{1,2}, Hyunjoon Song^{1,2}, Peidong Yang^{1,2} and Gabor A. Somorjai^{1,2}; ¹Department of Chemistry, University of California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California.

A general approach combining synthesis, characterization and reaction studies for the design of model high surface area heterogeneous catalysts has been developed. Well-defined (size and shape) Pt nanoparticles are synthesized and subsequently encapsulated in mesoporous silica. The resulting material is a high surface area catalyst containing nearly monodisperse particles. Influence of particle size and shape on catalytic activity and selectivity for various hydrocarbon hydrogenation reactions has been studied. Monodisperse Pt nanoparticles of 1.7-3.6 nm were synthesized by modified alcohol reduction methods using poly(vinylpyrrolidone) (PVP) as a surface regulating agent, while larger Pt particles (~7 nm) were synthesized in ethylene glycol (EG) solutions. Characterization of the particles confirmed they were spherical or slightly faceted. Pt particles of catalytically relevant size (~9 nm) with well-defined shape were synthesized by controlling the concentration of Ag ions in EG solutions. Pt cubes were synthesized at low Ag ion concentration, while cuboctahedra are obtained at higher concentrations. Further increase in the ion concentration led to octahedral Pt nanoparticles. Pt nanoparticles are encapsulated into mesoporous SBA-15 silica by the addition of templating polymer and silica precursor to the nanoparticle solution. The silica structure is hydrothermally synthesized in neutral conditions. The resulting Pt(1.7-7.1 nm)/SBA-15 catalysts were characterized by a number of physical and

chemical techniques. In order to expose the Pt surface, PVP and template polymer are removed. Thermogravimetric analysis of the catalysts demonstrates polymers are oxidized over a large temperature range. A standard protocol for catalyst activation involving oxidation and reduction treatment was developed. Characterization of the catalysts by chemisorption and ethylene hydrogenation confirmed that the polymers are removed by pretreatment. 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 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. The influence of particle shape on reaction selectivity was studied with crotonaldehyde hydrogenation. This study represents a new strategy in catalyst design that utilizes nanoscience to fabricate active sites, which are then encapsulated in a support to produce a model heterogeneous catalyst. The precise control obtained in these catalytic structures may enable the development of very accurate structure-activity and selectivity correlations.

9:00 AM **R4.4**

Unusual Catalytic Properties of Supported Silver and Gold Nanoparticles. Peter Claus¹, Seval Demirel-Guelen¹, Herbert Hofmeister², Christian Mohr¹ and Yucel Oenal¹; ¹Dep. Chemistry, Institute of Chemical Technology, Darmstadt University of Technology, Darmstadt, Germany; ²Max-Planck-Institute of Microstructure Physics, Halle, Germany.

Silver is well-known as industrial catalyst for oxidation reactions (synthesis of ethylene oxide, formaldehyde). Despite this fact, we have recently found excellent catalytic properties of supported silver nanoparticles in the hydrogenation of α,β -unsaturated aldehydes (i.e. acrolein). The selectivity to allyl alcohol was entirely different from that of conventional hydrogenation catalysts comprising Group 8-10 metals on non-reducible supports which do not produce unsaturated alcohols as main product in gas-phase hydrogenations [1-3]. Furthermore, the hydrogenation properties of supported silver nanoparticles with respect to the carbonyl group are unique because they are also able to hydrogenate only the C=O group of other polyfunctional organic compounds without simultaneous hydrogenation of, for example, aromatic or furan rings. On the other hand, while gold bulk metal is rather inert in chemical reactions and, thus, is of low interest for catalysis, highly dispersed gold particles (1-5 nm) on supports show surprisingly high activities in some heterogeneously catalyzed reactions. The CO oxidation at low temperatures is mainly used as model reaction to study the unusual properties of gold catalysts. However, to evaluate the catalytic potential of nanosized gold, other chemical reactions which allow to control also the selectivity have to be considered. Thus, reactions important to industry (hydrogenation of α,β -unsaturated aldehydes [4,5], liquid-phase oxidation of D-glucose and glycerol) has been selected by our group to study the particular catalytic properties of supported gold nanoparticles, especially the dependence of activity and selectivity on the gold particle size and morphology, called structure-sensitivity. It is important to note that elucidation of the active site issue of nanoscaled catalysts cannot be simply done by varying the size of gold particles, since the effects of faceting and multiply twinned particles may interfere. Advances of our group in developing new catalysts based on supported silver and gold nanoparticles will be highlighted by considering the parameters which control the selectivity. The results of catalyst characterization experiments (HRTEM, XPS, XAS, EPR) together with the kinetic and mechanistic information (TAP reactor) are discussed in correlation with the unusual catalytic properties of these catalysts. [1] P. Claus, H. Hofmeister, J. Phys. Chem. B 1999, 103, 2766. [2] W. Gruenert, A. Brueckner, H. Hofmeister, P. Claus, J. Phys. Chem. B 2004, 108, 5709. [3] M. Bron, E. Kondratenko, A. Trunschke, P. Claus, Z. Phys. Chem. 2004, 218, 405. [4] C. Mohr, H. Hofmeister, P. Claus, J. Catal. 2003, 213, 86. [5] C. Mohr, H. Hofmeister, J. Radnik, P. Claus, J. Amer. Chem. Soc. 2003, 125, 1905.

9:15 AM ***R4.5**

Catalysis by Metals: From Supported Nanoclusters to Single Crystals. David Wayne Goodman, Chemistry, Texas A&M University, College Station, Utah.

The electronic, structural, and chemical properties of unsupported metal and mixed-metal surfaces prepared either as single crystals or thin films have been detailed and contrasted with the corresponding properties of metal and mixed-metal nanoclusters. The latter vary in size from a few atoms to many and have been prepared on ultrathin single crystalline oxide supports of TiO₂, Al₂O₃, and SiO₂. An array of surface techniques including reaction kinetics of carbon monoxide oxidation and vinyl acetate synthesis have been used to correlate catalytic function of these surfaces with their physical and electronic

properties. Of special interest are the special physical and chemical properties that develop with metal cluster size reduction and/or metal-support interaction. Model studies of mixed-metal catalysts prepared by alloying Pd with Au, Cu, and Ag will be highlighted.

9:45 AM **R4.6**

Surface Defect-mediated Reactivity of Au/TiO₂(110).

Minghu Pan², Ken Taesung Park^{1,2}, Vincent Meunier³, William Shelton³, Sergei Kalinin⁴, Arthur Baddorf⁴ and E. Ward Plummer^{2,4}; ¹Physics, Baylor University, Waco, Texas; ²Physics and Astronomy, University of Tennessee, Knoxville, Tennessee; ³Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Metal clusters supported by transition metal oxides, as exemplified by the Au/TiO₂ system, have found broad applications as catalytic and sensor materials. The unusual properties of these systems originate from the specific interactions of metal clusters mediated by an oxide substrate, including local reduction below the cluster. In this work, we present recent results on the local interactions between one-dimensional defects on a TiO₂ surface and their reactivity with oxygen and Au nano-clusters studied by a combination of Scanning Tunneling Microscopy and Spectroscopy. High-resolution STM images, interpreted with first-principles theory, show that the observed one-dimensional strands have partially reduced Ti atoms coordinated at oxygen octahedral sites. When strands are exposed to 5×10^{-7} Torr O₂ at 300 K, oxygen is adsorbed and randomly nucleated on and along the strands. The results indicate the presence of exposed Ti ions that act as an active site for oxygen adsorption even at room temperature. Gold nano-particles of diameters 5 nm and less have also been deposited on the sub-stoichiometric rows of TiO_x and characterized by STM. Like point defects and step edges on TiO₂(110), the strands serve as nucleation sites for gold nano-clusters. The 1D defects of the surface are interpreted in terms of a surface crystallographic shear type structure, in contrast to the proposed Ti₂O₃ added row model by Onish and Iwasawa [Phys. Rev. Lett. 76, (1996) 791]. The implications of this behavior and specific interaction between gold clusters, defects and gas molecules for catalytic activity of the Au/TiO₂ system are discussed.

10:30 AM ***R4.7**

Energetics, Surface Reactions and Sintering of Nanoparticles: Size Effects. Charles T. Campbell, Chemistry, Univ. of Washington, Seattle, Washington.

In order to provide the energy needed for sustained industrial and economic development without causing serious environmental problems for human health, we must develop more efficient processes for a variety of chemical conversions. Catalysts consisting of metal nanoparticles supported on oxides hold great promise for many of these processes. We report here experimental studies of model catalysts consisting of structurally well-defined metal nanoparticles supported on single-crystalline oxide surfaces. We measure the chemical and catalytic reactivity and sintering kinetics of these nanoparticles as a function of their size. We also measure the energies of the metal atoms within the nanoparticles using adsorption microcalorimetry. This energy varies much more strongly than expected with particle size below 6 nm. This results in dramatic changes in the reactivity and sintering rates of the particles. The support oxide also exerts an important effect. The specific systems we will discuss include Au nanoparticles on TiO₂(110), which are active and selective catalysts in CO oxidation and propene epoxidation, Pd on alpha-Al₂O₃(0001), active for low-temperature methane combustion, and Cu, Ag and Pb nanoparticles on MgO(100). Particle sizes and number densities were measured by NC-AFM and STM. Chemical reactivity was measured by TPD and molecular beam / surface scattering. Catalytic activity was measured in a high-pressure cell attached to the surface analysis chamber. The adsorption energies of metal atoms were measured with a pulse molecular beam of metal and a pyroelectric polymer heat detector pressed against the backside of the single crystal. Sintering rates were measured by temperature-programmed low-energy ion scattering spectroscopy. * Supported by NSF and DOE-BES.

11:00 AM **R4.8**

Structural Changes of Bimetallic Pd_xCu_{1-x} Nanocatalysts Developed for Nitrate Reduction of Drinking Water.

Huiping Xu¹, Ray Twisten², Kathryn Guy², John Shapley², Anatoly Frenkel³, Duane Johnson² and Judith C. Yang¹; ¹Dept of Mat Sci & Engr, University of Pittsburgh, Pittsburgh, Pennsylvania; ²University of Illinois at Urbana-Champaign, Urbana, Illinois; ³Yeshiva University, New York, New York.

Reductive removal by hydrogenation using supported Pd/M bimetallic metallic catalysts has emerged as a promising alternative for the removal of many water contaminants including nitrate [1]. In

order to better understand how the atomic arrangement of Pd and a second element, such as Cu, affect the activity of nitrate reduction and selectivity of dinitrogen, we report a systematic study of novel PVP stabilized nanoscale Pd/Cu colloids with metal ratios ranging from 50:50 to 90:10 (Pd : Cu) by ex-situ and in-situ electron microscopy, including Z-contrast imaging [2], energy dispersive X-ray emission (EDX) and electron energy-loss spectroscopy (EELS) techniques [3], electron diffraction and high-resolution electron microscopy (HREM), and synchrotron x-ray spectroscopy. We found that a fairly uniform ensemble of Pd-Cu/PVP nanocatalysts predominantly exist over a broad range of composition from 50:50 to 90:10 (Pd: Cu) and the average particle size slightly increases from 3.3 to 5.2 nm with increasing amounts of Pd. A surprising abrupt change of the particle size occurs between 70 and 80 at% Pd, which may be relevant with nonhomogeneous distribution of both elements in Pd-Cu/PVP. We plan both in-situ electron microscopy and time-resolved x-ray spectroscopy in order to monitor the nucleation and growth of Pd-Cu/PVP nanocatalysts. In addition to this, we will apply theoretical analysis [4] to provide fundamental insights into this unusual particle growth behavior. [1]. A. Kapoor and T. Viraraghavan, *J. of Environmental Engineering*, 123, 371 (1997). [2]. A. Singhal, J.C. Yang and J.M. Gibson, *Ultramicroscopy*, 67, 191 (1997). [3]. K. Sun, J. Liu et al, *J. Phys. Chem. B* 106, 12239 (2002). [4]. D. A. Schwartz, N.S. Norberg, et al, *J. Am. Chem. Soc* 125, 13205(2003). Supported by the University of Pittsburgh, School of Engineering Heinz and Bevier Endowments.

11:15 AM R4.9

Preparation, Characterization and Reactivity of Nanoparticles Grown on Surfaces by Reactive Vapor Deposition. Jan Hrbek¹, J. Horn^{2,1}, Z. Song¹, D. Potapenko¹ and M. G. White^{2,1}; ¹Chemistry, Brookhaven National Lab, Upton, New York; ²Chemistry, SUNY Stony Brook, Stony Brook, New York.

A nanoparticle preparation technique coined Reactive Vapor Deposition is used for preparation of metal and metal compound nanoparticles on extended surfaces under vacuum. A single crystal surface is cooled to 90K and a multilayer of condensable reactant is grown on the surface. The condensed layer is exposed to a flux of metal atoms and slowly vaporized after the deposition. The stoichiometry and composition of the metal compound nanoparticles is dependent on the nature and thickness of the condensed layer while the nanoparticles morphology depends on the nature of the substrate, the layer thickness and the rate of layer evaporation. STM and XPS results for MoCx, MoSx and MoOx nanoparticles growth on a gold substrate will be discussed in detail and compared with results of other vacuum preparation techniques. Large number densities and a relatively narrow size distribution are among advantages of this technique. A general applicability of RVD for preparation of metal and metal compound nanoparticles on different substrates will be demonstrated by examples of the preparation of Ti compounds and Au clusters.

11:30 AM R4.10

Catalytic CO Oxidation with Gold and Platinum Loaded Free Standing Mesoporous Titania Films. Todd Aaron Ostome¹, Peter K. Stojmenov¹, Nathan R. Franklin^{1,2}, Eric W. McFarland² and Galen D. Stucky¹; ¹Chemistry and Biochemistry, UC Santa Barbara, Santa Barbara, California; ²Chemical Engineering, UC Santa Barbara, Santa Barbara, California.

Since the discovery of templated approaches to mesoporous materials in the early 1990's, there has been an incredible amount of research related to the fabrication of mesoporous transition metal oxides. Titania, an n-type wide band gap semiconductor, is already recognized by many as a promising material for heterogeneous catalysis, sensors, and photovoltaic energy conversion. In particular for oxidative catalysis, titania has been known to be an ideal host substrate for metal nanoparticles such as gold and platinum. Free standing 10 micron thick mesoporous titania films have been synthesized and impregnated with gold and platinum nanoparticles within the mesoporous architecture. These films have a continuous mesoporous structure which allows for optimal diffusion of reactant gases within the material. The gold and platinum loaded mesoporous titania films have been evaluated as catalysts for CO oxidation. Crystallinity of the titania matrix, metal particle size, and mesoporosity have been examined and optimized to determine their influence on catalytic CO oxidation.

11:45 AM R4.11

Preparation and Characterization of Highly Dispersed Catalytic Metal Oxide Nanoparticles by Localized Deposition in Mesoporous Silica. Bing Tan and Stephen E. Rankin; Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky.

Highly dispersed nanosized metal oxide particles are of particular

interests in catalysis, optics, and magnetics. For these applications, the product activity is determined not only by the size of the nano-scaled particles, but also by the dispersion of these particles on a porous support. Mesoporous silica has been widely used as a material support since it has high surface area, adjustable pore size, controllable pore structure, and is chemically inert. Metal nitrates, such as Fe(NO₃)₃, can be used to prepare iron oxide particles under basic conditions. The metal hydroxide precipitated from the process can be transformed to the oxide by calcination. In the traditional precipitation approach, the particles typically have large and irregular sizes. The reason may be the rapid, uncontrolled precipitation and agglomeration that occur after adding concentrated aqueous ammonia. Here, we improve the process of making dispersed nano-sized metal oxides by using amine-modified SBA-15 as the support. When placed in aqueous solution, protonation of the amine groups generates hydroxyl groups locally. The hydroxide reacts quickly with metal ions to produce iron hydroxide. At the same time, some of the metal ions may form complexes with amines or silanols at the surface of the material. By either mechanism, widespread rapid nucleation at the surface of the pores of the materials leads to the formation of well-dispersed metal oxide nanoparticles in the uniform cylindrical pores of SBA-15. As one example of this approach, we report the synthesis of dispersed iron oxide nanoparticles from iron (III) nitrate. Characterization by FTIR spectroscopy, transmission electron microscopy, energy dispersive x-ray spectroscopy, nitrogen adsorption, and x-ray diffraction shows that small (<10 nm) iron oxide particles line the walls of the pores of the support. The particles remain accessible and the loaded material maintains a high surface area, even at loading levels as high as 12 wt%. Superparamagnetic behavior at room temperature confirms the presence of nanoparticles with a diameter less than 16 nm. The catalytic activity of these materials for liquid-phase oxidation reactions will be discussed.

SESSION R5: Fundamental Phenomena of Photocatalytic Materials at the Nanoscale

Chair: James Gole

Tuesday Afternoon, March 29, 2005

Room 3001 (Moscone West)

1:30 PM R5.1

Synthesis and Photocatalytic Activities of HLaNb2O7/(Pt, Fe2O3) Porous Nanomaterials. Jihuai Wu, Yinghan Cheng and Jianming Lin; Huaqiao University, Institute of Materials Physical Chemistry, Quanzhou, Fujian, China.

HLaNb2O7 was prepared by the ion exchange reaction of KLaNb2O7 with 1 M HCl solution at 40°C for 72 h with two intermediate replacement of the acid in 24 h. KLaNb2O7 was obtained by calcining a stoichiometric mixture of K2CO3, La2O3 and Nb2O5 at 1150 °C in air for 24 h with one intermediate grinding. Pt and Fe2O3 were intercalated into the interlayer of HLaNb2O7 by the successive reactions of HLaNb2O7 with 0.6 mM [Pt(NH3)4]Cl2 solution for 72 h, 20 vol % of n-C6H13NH2/C2H5OH solution for 72 h at 70°C and [Fe3(CH3CO2)7(OH)(H2O)2]NO3 solution, followed by UV light irradiation. The sample obtained was designated as HLaNb2O7/(Pt, Fe2O3). The crystalline phases of the product was identified by XRD. The chemical composition of the sample was determined by TG-DTA analysis and ICP. The band gap energy of the product was determined from the onset of diffuse reflectance spectra of the powders measured. The specific surface areas of samples were determined by nitrogen gas adsorption method. The photoactivity of the catalyst was evaluated by measuring the volume of hydrogen gas produced from a 500 ml of 10 vol % methanol solution containing 1 g of dispersed catalyst under irradiation with a 200 W mercury lamp. These results suggested that the layered structure of HLaNb2O7 was retained after intercalation of n-C6H13NH2, Fe2O3 and Pt, although the distance of the interlayer changed. The gallery height of the pillar was less than 0.6 nm, which indicated the formation of porous nanomaterials. The photocatalytic H2 evolution was 8 cm³h⁻¹g⁻¹ using methanol as a sacrificial agent under irradiation with wavelength more than 400 nm from a 100-W mercury lamp. The photocatalytic activities of HLaNb2O7/Fe2O3 porous material is superior to those of Fe2O3 and is enhanced by the co-incorporation of Pt.

1:45 PM R5.2

Visible Light Photocatalysis via Nano-Composite CdS/TiO₂ Materials. Sessa S. Srinivasan, Jeremy Wade and Elias K. Stefanakos; Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida.

Nano-structured colloidal semiconductors with heterogeneous photocatalytic behaviour have drawn considerable attention over the past few years. This is due to their large surface area, high redox potential of the photogenerated charge carriers and selective reduction/oxidation of different class of organic compounds. Nano-structured TiO₂ is widely used as a photocatalyst for the

effective decomposition of organic compounds in air and water under UV radiation. On the other hand, the development of visible light activated photocatalysis, for utilizing the available solar energy remain a challenge and requires low band gap materials as a sensitizer. Among the various inorganic sensitizers, quantum-CdS with a small band gap ($E_g \sim 2.5$ eV) and an energetically high lying conduction band has been identified as a potential candidate. This can be coupled with a large band gap semiconductor (TiO_2 with $E_g \sim 3.2$ eV) for visible light photocatalysis and solar energy conversion. In the CdS sensitized TiO_2 nano-composite system, charge injection from the conduction band of the semiconductor sensitizer to that of TiO_2 can lead to efficient and longer charge separation by minimizing electron-hole recombination. In the present paper, we have carried out a systematic synthesis of nano-structured CdS/ TiO_2 via reverse micelle process. The structural and microstructural characterizations of the as-prepared CdS/ TiO_2 nano-composites are determined using XRD and SEM-EDS techniques. The visible light assisted photocatalytic performance is monitored by means of degradation of phenol in water.

2:00 PM R5.3

Raman Spectroscopy Analysis of Ultrathin Photocatalysis Titania Coatings by Chemical Vapor Deposition. Song Wei Lu, Caroline Harris, Walck D. Scott and Arbab Mehran; PPG Industries, Inc., Glass Technology Center, Pittsburgh, Pennsylvania.

Three commercially available ultrathin titania films on glass substrates, deposited by chemical vapor deposition (CVD), were analyzed by Raman Spectroscopy and X-ray diffraction (XRD) along with transmission electron microscopy (TEM) and atomic force microscopy (AFM). Utilizing Raman Spectroscopy, the phase of ultrathin titania films can be determined whether the films are on glass substrate or on an underlayer coating. In contrast, the phase of ultrathin titania films can not be clearly determined by XRD, especially when there is an epitaxial relationship with an underlayer. Photocatalytic activity by means of stearic acid degradation and hydrophilicity using water contact angle under UV irradiation of several commercial titania films will be discussed and compared.

2:15 PM R5.4

Deposition of Nanostructured Titania Films and Particles. Jorma K. Jokiniemi, Ulrika Backman, Unto Tapper and Ari Auvinen; Fine Particles and Catalysis, VTT Processes, Espoo, Finland.

Nanostructured TiO_2 films and particles were prepared in a tubular flow reactor at atmospheric pressure using titanium tetraisopropoxide as precursor. The morphology of the films and particles were characterized with scanning and transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy analysis of the deposits were also performed. Depending on the location of the substrate in the reactor i.e. the film forming species (vapour, monomers, particles), the morphology of the deposits was very different. A qualitative explanation is given for the different film morphologies. The formation and growth of the particles are also explained. Close to the inlet diffusion-controlled chemical vapour deposition took place resulting in a dendritic (leaf-like) structure. Once particles are formed in the gas phase, they deposit together with vapour resulting in granular, nanostructured films with incorporated particles. After the point where all the vapour is consumed separately, nearly monodisperse, 15 nm-sized particles deposited due to a competition between diffusion and thermophoresis. Downstream of the reactor porous deposits consisting of agglomerated nanosized particles formed [1]. The influence of the reactor temperature and the inlet precursor concentration on the morphology of the deposits was also investigated and is explained. The main applications for these nanostructured films are gas sensing devices and photocatalytic surfaces. References [1]. Ulrika Backman, Ari Auvinen and Jorma Jokiniemi (2004) Deposition of nanostructured titania films by particle assisted MOCVD, Surface & Coatings Technology, In press, Available online 27 April 2004.

2:30 PM R5.5

Photocatalytic Degradation of Methylene Blue in Periodic Mesoporous Nanocrystalline Anatase Films.

Moises A. Carreon¹, Sung Yeun Choi¹, Marc Mamak¹, Naveen Chopra² and Geoffrey A. Ozin¹; ¹Department of Chemistry, University of Toronto, Toronto, Ontario, Canada; ²Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

Here we present for the first time an adsorption and kinetic study of the photooxidative degradation of methylene blue in periodic mesoporous nanocrystalline hexagonal and cubic anatase (denoted meso-nc- TiO_2) thin films prepared via the EISA method. The photocatalytic degradation of methylene blue in meso-nc- TiO_2 films was found to follow first order kinetics with the decay rate constant decreasing with increasing analyte partial coverage. The adsorption (saturation coverage of the surface and adsorption affinity) and

photocatalytic (decay rate constant) parameters of these meso-nc- TiO_2 films were compared to conventional nanocrystalline anatase (denoted nc- TiO_2) films. The adsorption and photocatalytic parameters were related to the symmetry of the mesostructure and to the extent of crystallization of the photocatalytic active TiO_2 anatase phase. At comparable methylene blue coverages the rate and extent of photodegradation is superior for the meso-nc- TiO_2 films as compared to the conventional nc- TiO_2 films. The improved adsorption and photocatalytic properties of the meso-nc- TiO_2 films can be rationalized in terms of its higher surface areas, smaller primary crystallite size and the periodic ordered array of nanocrystals. Higher surface area enhances accessibility of the organic molecules on the meso-nc- TiO_2 . The ordered array of nanocrystals at the mesoscale leads to a better dispersion of the probe organic molecules in the host material. Smaller crystal size likely leads to higher exposure of the organic molecule to the photocatalytic active anatase phase.

3:15 PM *R5.6

Nanoscale Titania and C_{60} : From Environmental Impacts to Photocatalysis. Vicki L. Colvin, Chemistry, MS60, Rice University, Houston, Texas.

Traditionally, nanotechnology has been motivated by the growing importance of very small ($d < 50\text{nm}$) computational and optical elements in diverse technologies. Our effort has considered broadly how these features can be leveraged in environmental technologies. In one case, we have evaluated titania - a well known colloidal material with wide-ranging uses in paints, textiles and cosmetics. In its nanoscale form, titania exhibits both improved properties over its bulk form, as well as entirely new capabilities of great value in many environmental applications. This talk will discuss first the current approaches to the production of nanoscale titania in liquid phase reactions; control over the material size, shape and phase are critical variables in these synthetic methods. We have developed reactions which enable us to produce nanoscale rutile as well as anatase in a wide variety of shapes and sizes. Our current interest is in applying these materials to the problems of organic removal in contaminated water. We have evaluated the photocatalytic efficiency of these systems and shown improvements over commercially available photocatalysts. Finally, we have expanded our work on photocatalysts to include a new class of materials, the fullerenes. Their photochemistry and applications in water treatment will be presented.

3:45 PM R5.7

Advanced Photocatalysis with Anatase Nanocoated Multi-walled Carbon Nanotubes. Georgios Pyrgiotakis¹,

Sung-Hwan Lee¹, Vijay Krishna^{1,2}, Ben Koopman^{3,2}, Brij Moudgil^{1,2} and Wolfgang Michael Sigmund^{1,2}; ¹Materials Science and Engineering, University of Florida, Gainesville, Florida; ²Particle Engineering Research Center, University of Florida, Gainesville, Florida; ³Environmental Engineering Sciences, University of Florida, Gainesville, Florida.

Since 1972 when Fujishima and Honda discovered the photocatalytic split of water on titania electrodes under UV radiation, titania has been used in various photochemical applications ranging from photovoltaic cells to biological disinfection/purification. After UV irradiation and the electron hole pair generation a portion of the generated holes in the system are migrating to the surface where they create OH-Radical to oxidize organic materials. It has been shown that the coupling of TiO_2 with metals enhances the photocatalytic efficiency because the electrons flow to the metals and thus increases the amount of free holes by retarding electron-hole recombination. In this research a different approach is used to synthesize a photocatalytic nanocomposite, which utilizes the high aspect ratio of carbon nanotube (CNT) and the unique electrical properties to achieve higher photocatalytic efficiency. The particles were synthesized with sol-gel nanocoating on multi-walled carbon nanotubes (MWNTs). The nanostructure was characterized with the use of SEM, TEM, XRD, Raman, FTIR and UV-VIS spectroscopies. To determine and compare the photocatalytic efficiencies of commercial photocatalysts (Degussa P25) and TiO_2 nanocoated MWNTs, the organic Azo dye degradation tests were performed and the time required for 50% present reduction of the concentration was measured and used. Destruction was observed with UV-A and visible light irradiations. Also biocidal tests have been performed with bacteria (E. Coli) and spores (B. Cereus). The values used for comparison at those experiments were the D value and the LD-90 value. Results from dye degradation and biocidal tests signify TiO_2 nanocoated MWNTs have higher photocatalytic efficiency than the best photocatalysts in the market.

4:00 PM R5.8

Fabrication and Optical Characterization of Structures with High Surface to Volume Ratio in Sintered TiO_2 . David Maestre, Ana Cremades and Javier Piqueras; Física de Materiales, Universidad Complutense de Madrid, Madrid, Spain.

Due to the application of TiO₂ as a catalyst and as a gas sensor there is a high interest in the formation of structures of this material with a high surface to volume ratio. This includes the fabrication of nanostructures such as nanowires, nanoribbons or nanotubes which have been synthesized by different methods, often by thermal deposition on a substrate. However, nanostructures with high specific surface have been found to grow on the surface of different semiconductor materials, including several oxides, during sintering treatments. In the present work, this method has been used to fabricate nanostructures of TiO₂. The source is a disk of compacted TiO₂ powder which is also the substrate for the growth of the structures, which takes place under argon flow and at a critical temperature range near 1500 C. The effect of different thermal treatments on the formation and morphology of the nanostructures, the defect structure of the TiO₂ samples and the evolution of the luminescence properties are investigated by scanning electron microscopy, cathodoluminescence in the SEM and atomic force microscopy. Thermal treatments below 1450 C have not been found to produce changes in the flat surface of the grains, as observed in SEM. After annealing at 1500 C, elongated structures with cross-sectional dimensions from tens of nanometers up to several microns are formed on certain areas of the sample. Increasing annealing time and using different accumulative thermal treatments leads to the formation of different nanostructured features. In particular, samples formed by grains with a high number on nanosized terraces are obtained. The formation of the structures leads to changes in the luminescence behaviour of the sample. In particular, a near infrared emission at 1,52 eV is drastically reduced while a new band at 1,8 eV dominates the spectra after extended thermal treatments.

4:15 PM R5.9

Photocatalytic Effects of Nano-TiO₂ on Poly(Vinyl Butyral) Photo-Degradation. Leo Chau-Kuang Liao¹ and Ming-De Tong¹;

¹Chemical Engineering and Material Science, Yuan Ze University, Chung-Li, Taiwan; ²Chemical Engineering and Material Science, Yuan Ze University, Chjung-Li, Taiwan.

The raw materials of ceramic components usually consist of ceramic powders and organic materials, including solvent, dispersion, and polymer binders, such as poly(vinyl butyral) (PVB). In the manufacturing process, these organic materials have to be removed during thermal treatments in higher temperatures. However, the ceramic components can be seriously damaged if the conditions of the thermal treatments can not be operated and controlled properly. One of the reasons for the generation of the ceramic defect is due to an effect of decomposed gas evolved during the thermal degradation of the organics in higher temperatures. In this work, a novel method of PVB binder elimination was proposed using photocatalytic technique with the additive of nano-TiO₂ powders as a photocatalyst in lower temperatures. Different compositions samples of PVB and TiO₂ coated on different substrates are prepared to be used for the photo-degradation tests. These film samples were lighted with UV to evaluate the effect of the photocatalyst (TiO₂) on pvb photo-degradation for different periods of time. During the photo-treatment period, the organic composition of the samples was analyzed by FT-IR spectral data. Thermogravimetric analysis (TGA) was carried out to determine the organic composition of these samples left after the treatment. Besides, the surface structure images of the composite films were illustrated by SEM photos and the sample porosity was tested using a ASAP technique. Results show that the polymer can be almost removed by the photo-degradation process instead of using high temperature treatments. It indicates that nano-TiO₂ has a photocatalytic effect on the decomposition of a large molecular material from the data analysis. In addition, the kinetic analysis of PVB/TiO₂ photo-degradation was determined in this work.

4:30 PM R5.10

Semiconducting Chalcogenide Aerogels for Applications in Gas Sensing and Photocatalysis. Indika Arachchige, Jaya L. Mohanan and Stephanie L. Brock; Chemistry, Wayne State University, Detroit, Michigan.

Recently, we have developed a method for the assembly of metal chalcogenide nanoparticles into porous architectures using controlled surface decomplexation reactions accompanied by sol-gel processing and supercritical drying. The resulting chalcogenide aerogels exhibit porosity on the meso to macro scale, and are therefore appropriate for applications involving the entrance and egress of molecular species (photocatalysis, sensing, etc). In this paper, the role of synthesis and processing conditions on the surface area and optical properties of the chalcogenide aerogels will be presented and the activity of these materials for photocatalytic water splitting and gas-phase sensing, evaluated.

4:45 PM R5.11

Synthesis and Characterization of Photocatalytic TiO₂/ZnFe₂O₄ Nanoparticles. Jeremy Wade, Sessa S. Srinivasan and Elias K. Stefanakos; Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, Florida.

The wide bandgap semiconductor TiO₂, has become a dominant UV-activated photocatalyst in the field of air and water detoxification because of its high stability, low cost, high oxidation potential and chemically favorable properties. Nano-sized TiO₂ has attracted particular interest because of the unique effects associated with reducing particle size toward molecular phases, including shifting band edges to provide greater oxidation potentials and decreasing the surface area allowing more reactants to be adsorbed on the surface. In this paper, a new coprecipitation/hydrolysis synthesis route is used to create a TiO₂/ZnFe₂O₄ nanocomposite that is directed towards extending the photocatalytic activity of TiO₂ from UV to visible wavelengths. The effects of TiO₂'s accelerated anatase-rutile phase transformation due to the presence of the coupled ZnFe₂O₄ narrow bandgap semiconductor will be discussed. The transformations dependence on pH, calcination temperature, particle size, and ZnFe₂O₄ concentration has been analyzed using XRD, SEM, and UV-VIS spectrometry. The requirements for retaining the highly photoactive anatase phase present in a TiO₂/ZnFe₂O₄ nanocomposite are outlined. The visible light activated photocatalytic activity of the TiO₂/ZnFe₂O₄ nanocomposites have been compared to a reference Degussa P-25 catalyst using a solar-simulated phenol degradation reactor.

SESSION R6: Gas-sensing Mechanism in Nanoscale and Size-dependent Gas Sensing Properties

Chair: Stephanie Brock

Wednesday Morning, March 30, 2005

Room 3001 (Moscone West)

8:00 AM R6.1

High-Throughput Impedance Spectroscopy (HTIS) for the Characterisation of Nanoscaled Gas Sensing Materials.

Daniel Sanders, Maik Siemons, Tobias Koplín and Ulrich Simon; Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, NRW, Germany.

Semiconducting metal oxides are widely used as gas sensitive materials in sensor devices for process controlling, environmental monitoring as well as in domestic areas. Decisive parameters for the applicability of metal oxides as such materials are their sensitivity and selectivity towards a target analyte. Nowadays research often focuses on modification and optimisation of known materials. Our approach is to characterise the sensing properties of a large number of novel materials and compounds, aiming at the direct finding of novel gas sensor materials as well as the investigation of systematic effects by means of datamining. Therefore we developed a High-Throughput Impedance Spectroscopy (HTIS) screening system for the electrical characterisation of materials in variable atmospheres.[1,2] Using 64-electrode arrays, time consuming steps like calcination, conditioning and preliminary gas flow are parallelised, yielding in a throughput of more than one sample per hour for the characterisation at four different temperatures (typically 250°C - 400°C) and eleven individually composed reference- and testing gases. The material libraries under investigation are based on nanoscaled metal oxide particles with a diameter range from 20nm to 200nm, resulting from polyol mediated synthesis.[3] We optimised the synthesis towards parallelisation and to yield a high structural and compositional variety of oxides. Diversity in the libraries results from bulk- and superficial doping with halide-free metal salts and with size selected metal nanoparticles, respectively. The libraries sensitivities are deduced from impedance spectra, recorded in a frequency range from 10Hz to 10⁷Hz, by means of automated data fitting based on circuit equivalents. The HTIS and synthesis setup are presented. As an exemplifying result of this development a NO sensing material with almost fully suppressed cross-sensitivity towards NO₂ will be introduced. [1] U. Simon, D. Sanders, J. Jockel, C. Heppel, T. Brinz; J. Comb. Chem., (2002), 511 [2] A. Frantzen, J. Scheidtmann, G. Frenzer, W.F. Maier, J. Jockel, T. Brinz, D. Sanders, U. Simon, Angew. Chem. Intern. Ed. 43, (2004), 752 [3] M. Siemons, Th. Weirich, J. Mayer, U. Simon, Z. Anorg. Allg. Chem., (2004), 2083

8:15 AM R6.2

Silicon Nanocrystals: Photosensitizers for Molecular Oxygen.

Dmitri Kovalev, Physics Department, Technical University of Munich, Garching, Germany.

The energy transfer of electronic excitation plays an essential role in numerous scientific branches such as photophysics and biochemistry. To elucidate the fundamental physical effects occurring during energy transfer processes semiconductor nanostructures are viewed as a

promising approach. Recently, the photosensitization of molecular oxygen has gained considerable interest. Oxygen molecules in the electronic ground state are chemically inert due to their spin-triplet characteristic. However, excitation of an intermediate substance (photosensitizer) and subsequent transfer of energy to oxygen activates the molecule to an excited spin-singlet state. Activated singlet oxygen is shown to play very important role in chemical and biological processes. We report on energy transfer from excitons confined in silicon nanocrystals assembling nanoporous silicon layers or grains to oxygen molecules, being either physisorbed on the nanocrystal surface or present in the gas phase. Porous Si has huge internal surface area (up to 1000 m²/cm³) accessible for molecular oxygen and excitons confined in indirect bandgap silicon nanocrystals have very long radiative lifetime. Therefore the efficiency of the energy transfer from confined excitons to oxygen molecules is found to be almost equal to 100 %. Broad emission band of Si nanocrystals allows probing an exchange by individual spins between photoexcited Si nanocrystals and oxygen molecules in a wide energy range. Time-resolved measurements reveal the characteristic time of energy transfer to be in the range of microseconds. The modification of the surface termination of the nanocrystals allows controlling the efficiency of the energy transfer. The photosensitization of oxygen molecules in the gas and liquid phase at room temperature and their chemical reactivity is demonstrated. One of the most interesting examples is fast room temperature oxidation of silicon nanocrystal surfaces under their illumination by light. Finally we would like to discuss variety of possible applications of nanosilicon in photochemistry, biology and medicine.

8:30 AM *R6.3

Oxide Nanobelts for Electromechanical Coupled Nanosensors. Zhong L. Wang, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Piezoelectricity is an important phenomenon that characterizes the electromechanically coupled response of a material, and it has widely been used in science and technology. At nano-scale, most of the studies have been carried out for exploring the semiconducting properties of quantum dots, nanowires as well as nanotubes, but the nano-scale piezoelectric property remains an unexplored field until recently [1-6]. In our laboratory, we have synthesized a series of novel nanostructures of ZnO, a material that is semiconducting and piezoelectric. The piezoelectric coefficient of a piezoelectric nanobelt has been found to be almost tripled compared to the value of the bulk [7], clearly indicating the exciting applications of piezoelectric ZnO nanobelts for nano-scale electromechanical coupled sensors, transducers, switches and resonators. This talk will focus on our recent progress in investigating the growth, formation process and potential applications of piezoelectric nanobelts, nanorings and nanohelices. [1] Z.W. Pan, Z.R. Dai and Z.L. Wang, Science, 209 (2001) 1947. [2] W. Hughes and Z.L. Wang, Appl. Phys. Letts., 82 (2003) 2886. [3] X.Y. Kong and Z.L. Wang, Nano Letters, 2 (2003) 1625 + cover. [4] Z.L. Wang, X.Y. Kong and J.M. Zuo, Phys. Rev. Letts. 91 (2003) 185502. [5] Nanowires and Nanobelts - materials, properties and devices; Vol. I: Metal and Semiconductor Nanowires, Vol. II: Nanowires and Nanobelts of Functional Materials, edited by Z.L. Wang, Kluwer Academic Publisher (2003). [6] X.Y. Kong, Y. Ding, R.S. Yang, Z.L. Wang "Single-crystal nanorings formed by epitaxial self-coiling of polar-nanobelts ", Science, 303 (2004) 1348. [7] M. Zhao, Z.L. Wang, S. X.Mao, Nano Letters, 4 (2004) 587. [8] For details please visit <http://www.nanoscience.gatech.edu/zlwang/>

9:00 AM R6.4

Heterogeneous Porous Silica Thin Films Doped with NiO and Co₃O₄ Nanoparticles for Gas Sensing Applications.

Alessandro Martucci¹, Dario Buso¹, Massimo Guglielmi¹, Carlo Cantalini² and Mike Post³, ¹Ingegneria Meccanica Settore Materiali, Università, Padova, Italy; ²Chimica e Materiali, Università dell'Aquila, L'Aquila, Italy; ³ICPET, National Research Council of Canada, Ottawa, Ontario, Canada.

Nanoporous SiO₂ thin films doped with different functional oxide nanoparticles (NiO, Co₃O₄) have been synthesized by sol-gel methods on Si/Si₃N₄ substrates provided with Pt interdigital electrodes. The gas response to CO, NO₂, H₂ and CH₄ has been determined by optical and conductometric techniques. The nanostructure development of the heterogeneous films has been studied by X-Ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and Rutherford backscattering (RBS) spectroscopy. Typical SiO₂ film thicknesses and oxide nanoparticle sizes have been determined to be approximately 200nm and 5nm, respectively. Both NiO and Co₃O₄ nanocomposite films displayed a fast and reversible increase in optical transmittance in the VIS-NIR range (400-900nm) when exposed to CO. Conductometric techniques highlight a p-type response of both the oxides with decreasing resistance to NO₂ and increasing resistance to CO and H₂ respectively. The effect upon sensor response of parameters including

thermal annealing and residual porosity, metal oxide concentration, operating temperature (between room to 350 C temperature) and gas concentration has been studied. One key parameter to optimising sensor performance is matrix porosity. Data which demonstrates, compares and contrasts the sensor functionality of NiO and Co₃O₄ nanocomposites for CO, NO₂ and H₂ sensing will be presented.

9:15 AM R6.5

Hydrogen Sensors using Palladium Quantum Dots on Silicon Carbide for High Temperature Applications. Claudiu I. Muntele and Daryush Ila; Alabama A&M University, Normal, Alabama.

Silicon carbide is a promising wide-bandgap semiconductor intended for use in fabrication of high temperature hydrogen sensors or microelectronics applications running in hot environments without 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 for monitoring the surface morphology before and after implantation, 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 hydrogen 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 and 800 deg. 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.

9:30 AM R6.6

ZnO Nanostructures Synthesized via Double-Tube Vapor Phase Transport for Gas Sensing Applications. Yuxi Chen, Lesley Anglin Campbell and Weilie Zhou; Advanced Materials Research Institute, University of New Orleans, New Orleans, Louisiana.

One-dimensional ZnO nanostructures have received broad attention due to their distinguished versatile properties that are important for the potential applications in nanodevices and nanosensors. Particularly, ZnO nanostructure has been demonstrated to be a potential sensor for NH₃ and a photo-catalyst to reduce the emission of NO_x. In this presentation, double-tube vapor phase transport system is used to grow ZnO nanocombs, nanoblades and nanowires. The nanostructures in terms of growth temperature were investigated by electron microscopes. Vapor-solid (VS) growth mechanism dominates ZnO nanocomb formation at high temperature between 950oC and 980oC. With growth temperature decreasing, polar surface dominated anisotropic growth along the c-axis has occurred in ZnO nanocombs and nanoblades. The growth is controlled by the mixing of vapor-liquid-solid (VLS) and VS mechanisms. At low temperature between 710oC and 820oC, VLS controlled ZnO nanowire growth was directed by Au catalysts. The patterned ZnO nanowire arrays for gas sensing will also be discussed.

10:15 AM R6.7

Gas Sensing Properties of Nano-Crystalline Ba_xSr_{1-x}TiO₃ Thin Films – An Emerging Application. Somnath Chanda Roy¹, G. L. Sharma¹, M. C. Bhatnagar¹ and S. B. Samanta²; ¹Physics, Indian Institute of Technology Delhi, New Delhi, India; ²National Physical Laboratory, New Delhi, India.

Barium strontium titanate (Ba_xSr_{1-x}TiO₃) or BST thin films are being studied for their potential applications in high-density Dynamic Random Access Memories (DRAM), microwave devices, IR sensing and also as humidity and gas sensors. Although substantial progress has been made in the other areas, use of the BST films as gas sensors has not been explored beyond hydrogen[1]. In the present work, we report for the first time the ammonia sensing properties of BST thin films deposited by sol-gel technique. Literature review suggests that various thin films materials have been investigated for ammonia sensing application. These include films of polyaniline, elemental tellurium, MoO₃, InO₃ nanowires, (Cr,Ti)O₃, ZnO-In; which have been studied for application as ammonia sensors. But, although,

different types of materials mentioned above, have been used to fabricate ammonia gas sensors, most of these suffer from limited lifetime due to corrosive nature of ammonia gas. The use of BST films for ammonia sensing offers greater advantage due to superior insulating nature and higher chemical and thermal stability. Also, choice of the sol-gel as method of film preparation ensured easy tailoring of the microstructure through optimization of the process parameters. In the present work, the BST films were deposited on Si substrates with varying deposition conditions. Gold interdigitized electrodes were deposited on the film surface for gas sensing studies and measurements were done in the resistive mode. The structure and microstructure were studied with XRD and AFM, which revealed perovskite structure with nano-crystalline grain morphology. In our earlier works, it was shown that in sol-gel deposition process, the pre-sintering temperature[2] and pH of the precursor sol[3] has profound impact on the microstructure and dielectric properties of the films. Therefore, the ammonia sensing properties were studied as function of pre-sintering temperature, pH and also of film thickness, composition and the final sintering temperature. Also, the concentration of gas and the measuring temperature was varied to estimate the lowest detection limit and operating temperature for ammonia sensing. The BST films showed increase in resistance on exposure to ammonia gas. The sensitivity variation was from 20% to 60%, with lowest detection limit of about 160 ppm. The optimum temperature for operation was found to be close to 260°C. The selectivity studies were also performed with respect to other gases like ethanol, NO₂ and CO; in which BST films have been found to be selectively sensitive to ammonia. A mechanism of ammonia sensing based on the oxygen vacancy chemistry has been proposed and discussed. In this way, the present work has opened up a new avenue for the application of BST films. References 1.W Zhu et al, Sens Act B 65 (2000) 366-370 2. Somnath C Roy et al, Ceram Intl, 30,(2004),2283 3. Somnath C Roy et al,Appl Surf Sci,236,(2004),306

10:30 AM R6.8

Layer by Layer Composite Thin Films as Adsorptive, Gas Sensing Coatings. Nicole Zacharia and Paula T. Hammond; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The goal of this work is to explore the potential of dendrimer/semiconductor nanoparticle systems as the basis of highly sensitive chemical and biological agent sensors with high specificity. We are approaching this problem by using a unique polymer assembly approach (the layer by layer directed self-assembly process, or LbL method) to construct functional thin film protective coatings containing dendritic polymers and semiconductor nanoparticles as the basis of reactive or adsorptive protective coatings for fibers or fabrics. LbL is an inexpensive and versatile way to fabricate nanocomposite films with considerable control over the placement of many different components within the film's inner architecture. In this work we report the construction of PAMAM dendrimer/polyion thin films that very effectively adsorb half-mustard simulant, but still allow for high water permeability, a prerequisite for a coating meant for clothing. We believe these systems to show promise because of the large density of functional groups in the dendrimers, which can bind gas molecules. Titania/dendrimer multilayer thin films have also been developed, and their performance is currently under study. It is thought that these systems will also introduce reactivity of the half-mustard and allow breakdown into non-toxic components. We have previously demonstrated electrochromic properties in titania nanoparticle contained LbL films, and believe that both functionalities (protective and electrochromic) can be incorporated into a single film. Finally, an important new advancement has been made in the creation of a highly adsorbent carbon based nanoparticle with unusually high surface area. This carbon nanofoam system (CNF) has been surface modified for incorporation into the layer-by-layer thin films. Ultimate applications of this work are directed toward 1) the development of protective coatings that can be formed on fibers and/or fabrics at low cost, and will exhibit highly absorptive/reactive properties on exposure to a chemical agent, acting as an extremely efficient nanostructured protective layer; and 2) the formation of multi-component sensors based on the enhanced selectivity and sensitivity that can be achieved using semiconductor nanoparticles functionalized with the chemical groups presented by highly branched polymer structures designed to enhance selectivity toward specific chemical agents. The goal is to integrate the capability of detecting two, three or more separate agents within a single ultrathin film.

10:45 AM R6.9

Controlled Electrophoretic Patterning of Conducting Polyaniline from a Colloidal Suspension for Gas Sensing. Guofeng Li and Steve Semancik; Process Sensing Group, National Institute of Standards and Technology, Gaithersburg, Maryland.

We present a method for controlled deposition of conducting polyaniline from colloidal suspensions. Stable suspensions of

polyaniline colloids (~ 115 nm in diameter) were formed by dispersing polyaniline/formic-acid solution into acetonitrile. It was demonstrated that the positively charged polyaniline colloids can be electrophoretically deposited onto various substrate materials such as platinum and ITO, forming continuous ultra-thin films. We examined the effects of process parameters, such as deposition time, colloid concentration, and applied voltage, on the deposition efficiency. In addition, the deposited films were found to have a nanoporous microstructure that is ideal for gas sensing application. Furthermore, the efficacy of the technique was illustrated by electrophoretically patterning polyaniline onto selected individual micron-scale sensing elements within a microfabricated NIST microhotplate sensor array, and by further demonstrating its sensitivity to various gaseous analytes.

11:00 AM R6.10

TiO₂ Nanofibers Created by Gas Phase Reaction with H₂. Sehoon Yoo¹, Carmen M. Carney¹, Sheikh A. Akbar¹ and Ken H. Sandhage²; ¹Materials Science and Engineering, The Ohio State University, Columbus, Ohio; ²Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia.

The widespread utilization of nano-structured materials is often complicated by the conflicting demands for precise control of fine features (down to the nanometer scale) and for large-scale mass production. Recently, the authors' laboratory has led to the development of a novel and inexpensive technique creating oriented nano-fiber arrays of single crystal titania (TiO₂) by gas phase reaction with hydrogen. The nano-fibers are created by a selective and anisotropic etching process called "nano-carving". Unlike other nano-structure forming techniques, nano-carving doesn't require any sophisticated equipment. All one needs to produce the structure is a furnace for sintering the TiO₂ powder compacts (at 1200 °C for 6 h) and a controlled atmosphere furnace for a subsequent heat treatment (5% H₂/N₂ for 8 h at 700 °C). This process yields high surface area structures that are well attached to a substrate making them easy to adapt for industrial and commercial applications. The diameters of nano-fibers ranged from 15 to 50 nm and the lengths varied from 1 to 5 μm. Transmission electron microscope (TEM) with diffraction patterns showed that the direction of nano-fibers was [001]. The optimum conditions for nano-carving were 1100 - 1200 °C of sintering temperature, 680 - 740 °C of nano-carving temperature and over 500 ml/min of gas flow rate. Although nano-carving used reducing environment, the phase of nano-fiber was confirmed to be stoichiometric rutile TiO₂ from x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) results as well as selected area electron diffraction. The etching nature and the stoichiometry of nano-fibers are believed to result from fast Ti interstitial diffusion into bulk region. There are two pieces of evidence supporting Ti interstitial diffusion. The oxidation of nano-fiber sample above 600 °C created nano-pillars on the nano-carved surface. Also, nano-fibers didn't form on the surface of porous samples. For gas sensing applications, gold wires were attached onto the nano-carved surface and sensing signals were measured. The sensor showed good H₂ sensitivity up to the 2% range.

11:15 AM R6.11

Fabrication of Tin Oxide Nanowires by Chemical Vapor Deposition. Sun Sook Lee and Bethanie J. H. Stadler; Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota.

Nanostructured materials are of increasing importance because of their potential applications in areas such as electronics, optics, magnetics and energy storage. Tin oxide, an ionic metal oxide semiconductor, has been investigated for transistors, electrode materials, solar cell and gas-sensing device[1]. Nanostructured tin oxide will therefore be essential in reducing device sizes and increasing surface areas. Tin oxide nanowires have been prepared using several deposition technique including sol-gel[2], chemical deposition[3], and magnetron sputtering[4], but all of these techniques require a metal catalyst and rarely produce ordered arrays. In this work, ordered SnO₂ nanowire arrays were fabricated by chemical vapor deposition into templates of nanoporous aluminum oxide from a tin tert-butoxide source at 400 C. With this technique, it is not necessary to use a metal catalyst. SnO₂ nanowires were obtained that have diameters of 200-300 nm and lengths in the range of hundreds of nanometers to several tens of microns. The nanowires were uniformly assembled into the hexagonally ordered nanochannels of the anodic aluminum oxide membranes. As oxygen was added to the CVD system, the wires varied from pure tin to SnO to SnO₂. Subsequent anneals up to 900 C were sometimes used to obtain optimized crystallinity. The nanowires have been studied characterized by X-ray diffraction, scanning electron microscopy and element dispersion spectroscopy. The high surface areas of these nanowires make them of particular interest to gas sensors. 1. P. H. Wei, G. B. Li, S. Y. Zhao, and L. R. Chen, J. Electrochem. Soc. 1999, 146, 3536 2. E. R. Leite, I. T. Weber, E.

Longo, J.A. Varela, Adv. Mater. 2002, 12, 965 3. K.C. Song, Y. Kang, Mater. Lett. 2000, 42, 283 4. L.B. Fraigi, D. G. Lamas, N. E. W. de Reca, Mater. Lett. 2001. 47, 262

11:30 AM R6.12

Metal-Carbon Aerogel Nanocomposites Prepared via a Supercritical Deposition Route. Dafei Kang¹, Ying Zhang², Carl D. Saquing², Can Erkey² and Mark Aindow¹; ¹Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; ²Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Carbon aerogels (CAs) are novel mesoporous materials with tunable properties which make them ideal catalyst supports and an alternative to carbon blacks. Platinum/carbon aerogel (Pt/CA) and ruthenium/carbon aerogel (Ru/CA) nanocomposites for fuel cell and other applications were fabricated individually by supercritical carbon dioxide (scCO₂) assisted deposition of metal precursors followed by a controlled decomposition to give the elemental metal particles. Since carbon is essentially hydrophobic in nature, the non-polar CO₂ is expected to readily penetrate the interior of the porous CA, which may lead to a more uniform distribution of metal phase throughout the support. High-resolution TEM micrographs showed a rather narrow distribution of fairly monodisperse Pt and Ru particles throughout the bulk of carbon aerogel supports used. The nature and crystallinity of the particles were confirmed with XRD.

11:45 AM R6.13

Chemical Sensing with Polyaniline Nanofibers. Bruce Weiller¹, Shabnam Virji^{2,1}, Jiaying Huang² and Richard B. Kaner²; ¹Materials Processing and Evaluation Department, Space Materials Laboratory, The Aerospace Corporation, Los Angeles, California; ²Department of Chemistry & Biochemistry, Exotic Materials Institute and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California.

Polyaniline is a conducting polymer with electrical properties that can change greatly upon exposure to various chemicals. Most notably, when polyaniline is exposed to strong acids and bases, the conductivity changes by greater than 8 orders of magnitude. Recently, we have developed a simple, template-free chemical synthesis for polyaniline nanofibers. This interfacial polymerization is selective for nanofibers, can be readily scaled to make large quantities and can be controlled to selectively produce nanofibers with narrow distributions. Chemical sensors are fabricated from polyaniline nanofibers by casting films on microelectrode arrays. The nanofibers have significantly better performance than conventional material in both sensitivity and time response for all analytes tested including acids, bases, hydrazine, and organic vapors. Each of these gases produces a different response mechanism consisting of protonation, deprotonation, reduction, swelling, and conformational alignment, respectively. The high surface area, small diameter, and porous nature of the nanofiber films allow for facile diffusion of vapors, which is responsible for the enhanced performance. Most recently we have shown that additives can also be incorporated in the polyaniline matrix to detect analytes that do not give a significant response with unmodified polyaniline. Fluoroalcohol additives can be used for enhanced hydrazine detection and hydrogen sulfide can be detected using polyaniline nanofibers modified with metal salt additives. Therefore polyaniline nanofibers appear to be superior and versatile chemical sensor materials that have excellent potential for many chemical detection applications including homeland security.

SESSION R7: Sensing Device Configuration Using
Nanoscale Materials
Chair: Helmut Foell
Wednesday Afternoon, March 30, 2005
Room 3001 (Moscone West)

1:30 PM *R7.1

Giant Double-Layer Charge Injection Without Contacting Electrolyte: Properties Tuning and Device Applications. Dong-Seok Suh¹, Alan G. MacDiarmid¹, Edgar Munoz¹, W. Joshua Kennedy², Zeev V. Vardeny², Anvar A. Zakhidov¹, Vladimir Agranovitch¹, Alan B. Dalton¹, Steve Collins¹, Mei Zhang¹, Von H. Ebron¹, John P. Ferraris¹, Ali Aliev¹, Sergey Lee¹ and Ray H. Baughman¹; ¹Chemistry and NanoTech Institute, University of Texas at Dallas, Richardson, Texas; ²Physics, University of Utah, Salt Lake City, Utah.

We discovered a surprising generic method for charge-injection-based tuning of the bulk properties of electrolyte-free nanostructured materials over a wide range without incurring dopant intercalation and associated problematic structural changes. Specifically, we found

that carbon nanotube sheets, nanoporous metals, and other nanostructured materials, retain injected charge and associated structure and properties changes when non-faradaically injected with charge in a liquid-electrolyte supercapacitor and then removed from the electrolyte and dried in vacuum. Charge injection for carbon nanotube sheets in an electrochemical cell causes a quasi-parabolic order-of-magnitude increase in electrical conductivity, much of which is retained when the electrolyte is either evaporated or frozen. The implications of these discoveries are explored for diverse devices that function without electrolyte contact for electrochemically switched elements.

2:00 PM R7.2

Property of Nanoporous Anatase Titania Oxygen Sensor depending on Particle Size and Device Configuration. Yong-sang Cho¹, Markus Winterer² and Horst Hahn¹; ¹Material Science and Engineering, TU Darmstadt, Darmstadt, Germany; ²Department of Engineering, University Duisburg-Essen, Duisburg, Germany.

Metal-oxide semiconductors are predominant sensor material due to its low-cost, small scale and simplicity in function that the electrical conductivity depends on the ambient gas. However, in spite of its wide employment, it still suffers from some important disadvantages including unreliability at high temperature caused by structural transformation, cross sensitivity for some gases and long response time in some critical cases. Gas sensing properties are expected to be greatly improved, if the particle size could be reduced to extend the space charge layer over the entire nanoparticle or the entire neck portions of the grains. Moreover, as diffusion of oxygen through the conventional thin film takes much longer time than adsorption on the surface, making gas sensor with higher porosity and smaller particle size may be more beneficial, concerning easy gas permeation into the sensor film and negligible diffusion period due to small particle size, which leads to rapid gas detection. Stability of the sensor material during the operation may also be achieved using highly porous film, which has relatively low coordination number with neighboring particles. Since rutile is thermodynamically the most stable phase of titania, the majority of the researches have been concentrated on it, but recently anatase has become highly motivating because of its beneficial electronic properties including shallow donor level and high n-type mobility compared to rutile. Anatase titania nanopowders is produced by chemical vapor synthesis (CVS) method and their characteristics as gas sensor material is examined. The as synthesized powders with sizes of 5.5, 8 and 9 nm are perfectly crystalline, and each particle is nearly single crystal. Gas sensors are prepared from the CVS nanopowders on alumina substrates using silk screen printing or electrophoretic deposition. Two types of device configurations are used. One is typical interdigital structure, and the other is sandwich structure, in which the order of array is substrate / electrode / sensor film / electrode. Films are sintered at low temperature of 400 oC on the substrate to maintain the initial small size and to get sharp neck shape. The sensing behavior of titania nanopowder is studied by means of electrical conductivity measurement maintaining at the operating temperature from 250 oC to 350 oC in a dynamic test chamber, which supplies Ar and mixture of Ar and oxygen alternately. The gas sensing properties are examined as a function of particle size, different process parameters, and device configuration. Gas sensors with CVS-nanopowders showed improved sensitivity, response, recovery and full reversibility compared to sputtered thin film sensors. Sensor with smaller particle size and sandwich structure showed higher sensitivity. It is assumed that the nanoscale microstructure with high porosity, large surface area and the perfect crystallinity of the CVS powder are beneficial for the improved sensor properties.

2:15 PM R7.3

A Comparative Analysis: Localized and Propagating Surface Plasmon Resonance Sensors. Chanda Ranjit Yonzon and Richard P. Van Duyne; Northwestern University, Evanston, Illinois.

This work encompasses a comparative analysis of the properties of two optical biosensor platforms: (1) the propagating surface plasmon resonance (SPR) sensor based on a planar, thin film gold surface and (2) the localized surface plasmon resonance (LSPR) sensor based on surface confined Ag nanoparticles fabricated by nanosphere lithography. The binding of Concanavalin A (ConA) to mannose-functionalized self-assembled monolayers (SAMs) is chosen to illustrate the similarities and the differences of these sensors. A comprehensive set of non-specific binding studies demonstrate that the single transduction mechanism is due to the specific binding of ConA to the mannose-functionalized surface. Finally, an elementary (2x1) multiplexed version of an LSPR carbohydrate sensing chip to probe the simultaneous binding of ConA to mannose and galactose-functionalized SAMs is also demonstrated.

2:30 PM R7.4

Robust Nanostructured Gas Microsensor Platform from

Self-Organized Anodic Alumina. Dmitri Routkevitch, Oleg Polyakov, Debra Deininger and Clayton Kostelecky; Synkera Technologies Inc., Longmont, Colorado.

Nanostructured materials, with their small grain size, large number of grain boundaries, and high specific surface area, hold promise to enable significant performance benefits for solid-state gas sensors. To fully realize this potential, precision nanoscale engineering of the morphology and composition of sensing materials is needed. Furthermore, multiple challenges are associated with integration of nanostructured materials into reliable and manufacturable microsensors. This talk will overview our efforts on addressing these challenges by developing a novel gas microsensor platform based on anodic aluminum oxide (AAO). Anodic alumina, due to its self-organized nanostructured morphology, formed by uniform and parallel nanopores, is an attractive host for templated nanofabrication. This approach was pioneered independently by several groups, and is currently well recognized and widely used in both fundamental research and application development. Fabrication of gas microsensor from AAO includes several key steps: (1) synthesis of nanoporous anodic alumina with required morphology and thickness; (2) micromachining of sensor substrate equipped with microheater and sensing electrodes; (3) conformal deposition of high surface area (up to 100 m²/g) nanostructured sensing materials onto the walls of the nanopores with extremely high aspect ratio, and (4) sensor packaging. The resulting sensor architecture, formed by high surface area (up to 100 m²/g) arrays of nanotubes of sensing materials intrinsically integrated into micromachined ceramic substrates, has numerous intrinsic advantages over conventional sensors. We will review these steps and discuss the effects of sensor design, specific surface area, deposition processes and other factors on sensor fabrication and performance. Described microsensor platform enables sensors that have low thermal mass and low power consumption, broadens the operating temperature range, and provides capability of regeneration by internal heating to high temperature. In many cases it also improves response time, sensitivity and selectivity. Several types of low-power gas microsensors and sensor arrays are currently under development at Synkera Technologies using presented platform. These include metal oxide conductimetric, catalytic combustion and electrochemical sensors. Case studies will be presented. This work was supported by DOE (DE-FG03-99ER82842, DE-FG03-99ER82839), NSF (DMI-9861546), NIH (1R43-ES10739) and NIST (SB1341-02-W-1073) 1. D. Routkevitch, P. Mardilovich, A. Govyadinov, S. Hooker, S. Williams, Nanostructured Ceramic platform for Micromachined Devices and Device Arrays- US patent No 6,705,152 B2, granted 03/16/04; filed 05/07/1999.

2:45 PM R7.5

Detection of NO₂ Down to ppb Levels using Individual and Multiple In₂O₃ Nanowire Devices. Daihua Zhang, Zuqin Liu, Chao Li and Chongwu Zhou; EEEP, University of Southern California, Los Angeles, California.

We demonstrate detection of NO₂ down to ppb levels using transistors based on both single and multiple In₂O₃ nanowires operating at room temperature. This represents orders-of-magnitude improvement over previously reported metal oxide film or nanowire/nanobelt sensors. A comparison between the single and multiple nanowire sensors reveals that the latter have numerous advantages in terms of great reliability, high sensitivity and simplicity in fabrication. Furthermore, selective detection of NO₂ can be readily achieved with multiple-nanowire sensors even with other common chemicals such as NH₃, O₂, CO and H₂ around.

3:15 PM *R7.6

Inorganic Nanotube Based Ionic Transistors. Peidong Yang and Arun Majumdar; Univ. Calif. Berkeley, Berkeley, California.

Solutions exhibit novel properties when they are confined to regions comparable to either the ionic/molecular size or the Debye screening length of the electric double layer. Here we report a nanofluidic transistor, a three-terminal device with a gate electrode, that exploits such confinement effect and uses it for electrostatic control of ionic and molecular transport in nanofluidic channels. Direct evidence of how the gate voltage modulates ionic and molecular concentration in the channel, and controls their transport will be discussed. This effect is similar to the field effect modulation of electrons and holes in a metal-oxide-semiconductor (MOS) transistor. Furthermore, these nanotube transistors provide a novel platform for probing and electrostatic manipulation of the chain dynamics of single DNA molecules within nanochannels. A new phenomenon, an ionic current crossover during DNA translocation, was discovered. These results illustrate the efficacy of field-effect control in nanofluidics, which would have broad implications on integrated nanofluidic circuits for manipulation of ions and biomolecules in femtoliter volumes.

3:45 PM R7.7

Nanoscale Electronic Nose for CO and SO₂ Detection. Arun Kumar¹, Brian Brantley² and Ashok Kumar^{1,2}; ¹Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida; ²Department of Mechanical Engineering, University of South Florida, Tampa, Florida.

Carbon monoxide and sulfur dioxide are common exhaust emissions generated by automobiles and industry processes. Carbon monoxide is widely known as a colorless, odorless gas which is one of the major causes of death and accidental poisoning. Sulfur dioxide is an equally important gas emission generally creating respiratory ailments and contributes to acid rain. With the ever increasing global industrialization, these harmful gases are being produced at an alarming rate causing much concern for human and environmental health. The current sensor approach aims to detect these gases using a conjugated nanoparticle consisting of a functionalized polymer and catalyst. The use of nanoparticles enables the simultaneous detection of these gas species at low concentration (ppb) levels without interference. Modified nanoparticles are attached with two main square regions of 0.5 by 0.5 microns to fabricate nanosensor array using lithographic technique. In the current approach, gold and platinum nanoparticles were used as catalyst materials in conjunction with the functionalized conducting polymers. Polypyrrole and polyaniline in conjugation with nanoparticles are selected to develop a more specific and selective sensor array for carbon monoxide and sulphur dioxide detection at ppb level. The modified nanoparticles are characterized with SEM, FTIR and XRD. Further experiments are under progress in our laboratory to develop a highly sensitive electronic nose.

4:00 PM R7.8

From Nanostructures to Porous Silicon: Sensors, Photocatalytic Reactors and Battery Electrodes. James L. Gole^{1,2}, Steven Lewis¹ and Peter Hesketh²; ¹School of Physics, Georgia Institute of Technology, Atlanta, Georgia; ²School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Porous interfaces are transformed within the framework of nanotechnology to develop highly efficient sensors, interactive support surfaces, active battery electrodes, and nanophotocatalytic frameworks. A rapid, reversible, and sensitive porous silicon (PS) gas sensor, based upon a uniquely formed highly efficient electrical contact to a nanopore covered microporous array, is modified to introduce selectivity and for the purpose of creating a novel heterogeneous photocatalytic reactor. Further, this PS surface, properly prepared, forms an active Li-battery electrode. Photoluminescence induced metallization is used to obtain a highly efficient electrical contact as we demonstrate the detection of HCl, NH₃, CO and NO at the ppm level. The device, which operates at a bias voltage of 1-10 mV, resulting from a low resistance, 20Ω, contact, also forms the basis for more efficient electroluminescent devices. Electroless gold and tin treatments selectively modify the impedance response of the device to considerably improve detection for NH₃, CO, and NO. Through FFT analysis, a gas response can now be acquired and filtered on a drifting baseline, further increasing sensitivity. These sensor suites are now being extended to develop microreactors in which nanoscale silica² and titania³ based quantum dot (QD) photocatalysts will be placed within the pores of PS and excited using PS electroluminescence or photoluminescence to excite visible light absorbing QDs. Highly efficient light absorbing titania-based QDs have been developed. Using a nanoscale exclusive synthesis route, we directly treat TiO₂ nanocolloids and, in seconds, at room temperature, we produce nitrogen doped, stable, and environmentally benign TiO_{2-x}N_x photocatalysts whose optical response, now not limited to the ultraviolet, can be tuned across the entire visible region. This synthesis, which can be simultaneously accompanied by metal atom seeding, can be accomplished through the direct nitration of anatase TiO₂ nanostructures with alkyl ammonium salts. Tunability throughout the visible depends on the degree of TiO₂ nanoparticle agglomeration and the influence of metal seeding. No organics are incorporated into the final TiO_{2-x}N_x products. These visible light absorbing photocatalysts readily photodegrade methylene blue and gaseous ethylene. They can be transformed from liquids to gels and placed on the surfaces of sensor and microreactor based configurations 1) to produce an improved photocatalytically induced solar based sensor response, and 2) with a goal to facilitate catalytically induced disinfection of airborne pathogens. In contrast to a nitridation process which is facile at the nanoscale, we find little or no direct nitridation of micrometer sized anatase or rutile TiO₂ powders at room temperature. Thus, we demonstrate an example of how a traversal to the nanoscale can vastly improve the efficiency for producing important submicron particles.

4:15 PM R7.9

Formation of Silver Nanoparticles in Sputtered Silver Oxide

Layers and Molecular Sensing by Them. Makoto Fujimaki¹, Yasuhiko Iwanabe^{1,2}, Koichi Awazu¹ and Junji Tominaga¹; ¹Center for Applied Near-Field Optics Research, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan; ²Graduate School of Engineering, Tokyo Denki University, Chiyoda, Tokyo, Japan.

High-sensitivity molecular-detection sensors, which are able to detect a small quantity of a specific molecule, have been anxious in medical, biotechnological, and ecological fields. We developed a molecular detection sensor utilizing surface-enhanced Raman scattering (SERS) by silver nanoparticles formed in sputtered silver oxide layers [1,2]. This sensor is able to detect 10^{-8} M molecules in a solvent, and the detection area is as small as $1\mu\text{m}^2$. Because of these capabilities, this sensor is expected to be a good sensing tool in the above-mentioned fields. In the present research, we have observed SERS efficiency of silver nanoparticles formed by laser irradiation or thermal annealing in sputtered silver oxide layers. Silver nanoparticles formed by Ar⁺ laser (488 nm) or He-Ne laser (633 nm) irradiation show good SERS effect, while signal enhancement is not observed in silver nanoparticles formed by thermal annealing at 600 °C for 5 minutes. These results indicate that the laser irradiation forms silver nanoparticles in a better shape with effective density. [1] USP 6,707,549 B2 [2] D. Buchel, C. Mihalcea, T. Fukaya, N. Atoda, and J. Tominaga, *App. Phys. Lett.* 79, 620-622, (2001).

4:30 PM R7.10

Hydrogen Gas Sensing using Nanoporous SiC.

Timothy J. Fawcett¹, John T. Wolan¹, W. J. Choyke³ and Stephen E. Sadow²; ¹Chemical Engineering, USF, Tampa, Florida; ²Electrical Engineering, USF, Tampa, Florida; ³Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania.

A hydrogen gas sensor fabricated on the surface of nanoporous SiC has been experimentally evaluated. The resistive gas sensor structure consists of planar ohmic contacts formed on the surface of nanoporous n-type 4H-SiC 8 deg off-axis towards the [1 1 -2 0] direction. Non-porous samples from the same SiC wafer were also tested for comparison. The nanoporous SiC layer was formed via UV assisted electrochemical etching, producing a 10 μm thick porous layer with a "dendritic" morphology. The sensors were exposed to hydrogen concentrations ranging from 0.05% (500 ppm) in either N₂ or Ar to 100% H₂. These gas sensors were tested at temperatures ranging from 25C to 500C. The sensors produced reversible and repeatable responses to all concentrations of hydrogen tested in this study. Experiments were conducted to shed light on the kinetics of adsorption and desorption of H₂ from the nanoporous SiC surface and these preliminary results will be presented.

4:45 PM R7.11

Engineering of Porous, Tin Oxide Nanoparticle Microshells for Sensor Applications. Carlos J. Martinez¹, Christopher Montgomery¹, Bernard Hockey² and Steve Semancik¹; ¹Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland; ²Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland.

We have sought to enhance the sensitivity of conductometric gas sensors through the design and fabrication of porous, three-dimensional tin oxide nanoparticle films. These films were fabricated via the self-assembly from solution of nanoparticle-decorated latex microspheres, which serve as sacrificial templates. Through heating, the latex microspheres were removed to reveal a porous 3-dimensional structure composed of interconnected hollow nanoparticle microshells with ultra-thin walls. These structures include macropores (50 nm - 1000 nm) on the inside and between the microshells, and micropores (< 2 nm) and mesopores (2 nm - 50 nm) within the shells. The multiscale porous architecture promotes analyte diffusion and maximizes available active surface area. Sensor measurements were performed by depositing these films onto MEMS microsensor platforms with embedded inter-digitated electrodes and heaters. We report on film conductance changes measured at different temperatures, caused by exposure to test gases (CO, H₂O, MeOH) in a dry air background. Special attention was placed on understanding the influence that structural factors (film thickness, packing density) have on the sensitivity, selectivity, stability and response time of these materials. We also compare the performance of these high surface area films to compact microporous nanoparticle films and CVD SnO₂ films. The nanoparticle microsphere films exhibited partial selectivity to different gases, good dynamic range at different temperatures and concentrations, as well as good repeatability and stability over long runs. Increases in sensitivity to test analytes are discussed in terms of enhanced surface area for adsorption and efficient transport of analyte to the surface sites.

SESSION R8: Poster Session: Nanoporous and Nanostructured Materials for Catalysis, Sensor, and Gas Separation Applications

Chairs: James Gole and Song Wei Lu

Wednesday Evening, March 30, 2005

8:00 PM

Salons 8-15 (Marriott)

R8.1

Abstract Withdrawn

R8.2

Transferred to R7.2

R8.3

All-optical Chemical Gas Sensors for Harsh Environments Based on Au-YSZ Nanocomposite Films. George Sirinakis,

Rezina Siddique, Zhouying Zhao and Michael A. Carpenter; College of Nanoscale Science and Engineering, University at Albany, Albany, New York.

Growing environmental concerns associated with the use of fossil fuels have necessitated the development of a new approach to energy generation that is based on the synergistic operation of existing and developing power systems such as turbines and solid oxide fuel cells (SOFC). In the specific case of the Turbine/SOFC hybrid system, sensors for the detection of H₂, CO, sulfur compounds, and hydrocarbons under harsh oxidizing and reducing environments in the temperature range between 600 and 900°C are urgently needed. Nanocomposite films comprised of metal nanoparticles embedded in various oxide matrices have attracted significant scientific and technological interest as high temperature optical gas sensors due to their unique optical properties. In this work YSZ-Au nanocomposite films were synthesized from a YSZ and a Au target by the radio frequency magnetron co-sputtering technique in combination with a post-deposition annealing treatment in an argon atmosphere, with the annealing temperature being varied from 700-1000 °C in steps of 100 °C. UV-Vis absorption spectroscopy is employed to evaluate the feasibility of using the surface plasmon resonance bands of embedded Au nanoparticles in a YSZ matrix for the detection of CO at operating temperatures up to 800 °C. X-Ray Diffraction spectroscopy (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques are used for Au particle size measurements in order to correlate the changes in the optical signature of the nanocomposite films with the average Au particle size and elucidate the underlying sensing mechanisms.

R8.4

Gas Sensing Properties of Tin Oxide Powder Synthesized in Presence of Surfactants. Kiran Jain¹, Ms. Rashmi² and S. T.

Lakshmikumar¹; ¹Electronic Materials Division, National Physical Laboratory, New Delhi, India; ²Materials Characterization Division, National Physical Laboratory, New Delhi, India.

Sensitive and precise gas sensors are becoming essential for industrial processes, environment monitoring, and smart systems. SnO₂ based gas sensors are widely used to detect reducing gases such as in gas leak alarms, in pollution emission control and in alcohol concentration monitoring. The increases of conductance of SnO₂ caused by the surface reactions between pre-adsorbed surface oxygen species and reducing gases are used to detect the concentrations of reducing gases. Since the reaction between surface oxygen species and the reducing gases is of importance for gas sensitivity, the gas sensitivity can be improved by increasing the surface area, or decreasing the particle size. Nanocrystalline powder will provide more surface sites for more oxygen to be adsorbed and contacted with the gases. Preparation of SnO₂ powder with minimum variation in particle characteristics is of profound importance for the thick film formulation to achieve the best rheology and morphology of the structure. A variety of methods such as sol gel, chemical vapor deposition magnetron sputtering, evaporation of elemental tin in an oxygen atmosphere decomposition of the organometallic precursor, hydrothermal synthesis and sonochemical method have been used to prepare SnO₂ particles and films. In the present investigation, we have made efforts towards reduction in particle size using a process wherein surfactants were added to the reactants in order to improve the properties of SnO₂ powders. Nanocrystalline tin oxide powder was prepared using a solution precipitation technique after adding various surfactants, such as sodium dodecyl sulphate, Triton X-100 and AOT. Thick films were prepared by screen-printing technique, and tested for their gas sensitivity towards LPG and CNG at various temperatures and concentrations. Powders were characterized using XRD, SEM, TEM for their particle size and morphology. To develop a stabilized gas sensor, calcinations and sinterings were done at 600 and 800 °C respectively. An improvement in gas sensitivity and a decrease in

response time was observed for the powders prepared in presence of surfactants as compared to without surfactants.

R8.5

Gas Sensing in Nanostructured Perovskite $\text{Sm}_{0.9}\text{Ba}_{0.1}\text{CoO}_{3-y}$ Prepared by a Solution Method. Carlos R. Michel, Emilio Delgado and Arturo Chavez; Physics, Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

Intensive scientific research on new inorganic materials for applications in areas of gas sensors, heterogeneous catalysis, gas separation and cathodes for solid oxide fuel cells, has been focused in some oxides possessing the perovskite-type structure. Among these oxides, some cobaltites have been widely studied due to their high ionic conductivity and high chemical activity; specially those corresponding to members of the solid solutions: $\text{M}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ ($\text{M} = \text{La}, \text{Nd}$). The partial substitution of M cations by strontium in these perovskites, makes that cobalt ions have a mixed-valence state: Co^{2+} and Co^{3+} , which enhances the transport and catalytic properties. In this work, polycrystalline samples of $\text{Sm}_{1-x}\text{Ba}_x\text{CoO}_{3-y}$ ($x = 0, 0.1$) were prepared by a solution method, using stoichiometric amounts of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ in aqueous media. In order to identify the temperature of formation of these oxides, the precursor resins obtained after drying the mixtures at 76°C , were analyzed by DTA and TGA, from room temperature to 1150°C . The structural evolution whereas increasing calcination temperature was analyzed by X-ray powder diffraction. From these results, single-phase SmCoO_{3-y} was obtained at 900°C , whereas pure $\text{Sm}_{0.9}\text{Ba}_{0.1}\text{CoO}_{3-y}$ was synthesized at a temperature as low as 700°C . For the former, micron-sized particles were observed by SEM; and for the latter, a nanostructured and nanoporous material was clearly identified by TEM. The particle size for $\text{Sm}_{0.9}\text{Ba}_{0.1}\text{CoO}_{3-y}$ was approximately 80 nm, and this size was increased by sintering processes, to study the relationship between sensing behavior and particle (and porous) size. DC electrical conductivity measurements were performed in air, O_2 and CO_2 , on thick films prepared with those oxides; the selected temperature range was from 50°C to 650°C . The resulting gas sensitivity vs. temperature graphs showed a moderate gas sensing capability in these materials; however, an improvement of this property was observed for samples with smaller particle size.

R8.6

Ag Doped WO₃ films for Gas Sensing Studied by High Resolution Photoelectron Spectroscopy. Carla Bittencourt¹, F. Mirabella¹, P. Ivanov², E. Llobet², M. A. P. Silva³, L. A. O. Nunes³ and J. J. Pireaux¹; ¹LISE/FUNDP, University of Namur, Namur, Belgium; ²Departament d Enginyeria Electronica, Universitat Rovira i Virgili, Tarragona, Spain; ³Instituto de Fisica de Sao Carlos, University of Sao Paulo, Sao Carlos, Brazil.

It is known that the addition of noble metal atoms in WO₃ matrix enhances the gas sensing properties of this material. In spite of the numerous studies on the performance benefits, little information exists about the origin of these improvements, particularly about the real structural and electronic modifications introduced by noble metal addition in the sensor. In this work, the morphology, vibrational spectra and electronic properties of WO₃ films loaded with different Ag levels were investigated. The films were prepared by screen printing onto Si substrates and annealed in air at 600°C . AFM micrographs recorded on the samples reveal that the surfaces of the films are essentially inhomogeneous, and made up of grains and voids. The grain size increases with the Ag loading level. The observation of a Raman band near 930 cm^{-1} suggests the formation of a AgxWO₃ bronze structure that can have been formed by intercalation of Ag into WO₃ tunnels resulting in a more stable film. X-ray photoelectron spectroscopy was performed using a ESCA-300 (SCIENTA, Sweden) photoelectron spectrometer, with a nominal resolution (source + analyser) of 0.4 eV. The concentration of the silver inferred by XPS is 1.8 times larger than the nominal concentration for all samples suggesting that the Ag atoms are preferentially at the WO₃ grains surface. To best reproduce the W 4f core level spectrum, three doublets are necessary; they correspond to tungsten atoms with oxidation state +6 and +5 (4f_{7/2} localized at 35.7 eV and 34.7 eV respectively) while the third doublet at 36 eV is associated to surface defects (oxygen vacancies). For increasing Ag doping level, surface defects and W+5 states decrease, supporting the assumption that the peak at higher binding energy is associated with oxygen vacancies: indeed, during the annealing Ag atoms probably migrate to defect sites changing the electronic density near the W atoms compensating the oxygen vacancies. A structure at 32 eV is associated with photoelectrons emitted from tungsten atoms involved in the AgxWO₃ bronze formation. In order to determine if any quantitative change was induced in the valence band by hybridization of Ag and WO₃ states, a numerical procedure to reproduce the valence band of the WO₃ film and an Ag metal layer was performed: no strong electronic interaction between the Ag atoms and the WO₃ grains was found. Sensors fabricated with WO₃:Ag films exhibited a significant increase

in their sensibility and selectivity towards NO₂ detect.

R8.7

Synthesis of Tin Oxide Nanoparticles Using a Mini-arc Plasma Source. Ganhua Lu^{1,3}, Junhong Chen^{1,3} and Marija Gajdardziska-Josifovska^{2,3}; ¹Mechanical Engineering, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin; ²Physics, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin; ³Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin.

Miniaturized electronic noses to rapidly detect and differentiate trace amount of chemical agents are extremely attractive. Use of tin oxide nanoparticles doped with various materials as sensing elements has been proved to significantly improve both the response time and the sensitivity of gas sensors or electronic noses. In this paper, we report the synthesis of pure and doped tin oxide nanoparticles using a simple, convenient, and low-cost mini-arc plasma source. The reactor consists of a tungsten cathode and a graphite anode housed in a chamber constructed with swagelok tubing fittings and quartz tube and the arc is powered by a commercial tungsten inert gas (TIG) welder. Pure or doped tin oxide nanoparticles are produced by evaporation of solid tin or tin alloy in the arc source followed by rapid quenching and oxidation. The nanoparticle size distribution is measured online using a scanning electrical mobility spectrometer (SEMS). Periodically, the product nanoparticles are sampled and analyzed ex-situ by high resolution transmission electron microscope (HRTEM) for morphology, energy dispersive X-ray spectroscopy (EDX) for composition, and X-ray diffraction (XRD) for structure. Tin oxide nanoparticles with sizes ranging from a few nm to a few tens of nm have been produced. TEM and XRD analyses show that most nanoparticles as produced are spherical, nonagglomerated, and crystalline. The generic method may also be used to produce nanoparticles of many other materials for next-generation nanoparticle-based devices using the bottom-up approach.

R8.8

Long-Term Stability of the Thermally-Carbonized Porous Silicon Humidity Sensor. Jaani Tuura, Mikko Bjorkqvist, Jarno Salonen and Vesa-Pekka Lehto; Laboratory of Industrial Physics, University of Turku, Turku, Finland.

Since the first reported prototype of thermally-carbonized porous silicon (TCPSi) humidity sensor [1], a lot of work has been done to optimize the properties of such sensor. Annealing has been taken into processing steps, because it diminishes hysteresis due to pore size enlargement in porous silicon (PSi). A drawback of annealing is, that sensitivity of the sensor is decreased [2]. However, the sensitivity is still several hundreds of percents. To improve the stability and treatment efficiency, the carbonization procedure contains now a two step thermal treatment of the sensors. In the first part of the treatment, low temperature (500°C) and continuous flush of acetylene and nitrogen gas mixture have been applied to obtain hydrocarbon termination to the surface. Second part is immediate high temperature (820°C) treatment with nitrogen flush. So, that the silicon carbide surface is formed. In present study, the long-term stability of TCPSi humidity sensors has been investigated. Studies show only small changes in characteristic behaviour of the sensors. After three months storage in room atmosphere, sensors seems to be fully stabilized and the variation of the capacitance values for the humidities are negligible. Decline of the sensitivity during storage has been found to be about 37 %, still giving over 200 % sensitivity. Hysteresis as well as response time to humidity changes due to ageing have also been discussed. [1] M. Bjorkqvist, J. Salonen, J. Paski and E. Laine, Sensors and Actuators A 112, 244-247 (2004). [2] M. Bjorkqvist, J. Paski, J. Salonen and V.-P. Lehto, IEEE Sensors Journal, accepted (2004).

R8.9

Nanomagnetic Ni Array in Porous Silicon as a Possible Magnetic Field Sensor in the High Field Range up to 7 T. Petra Granitzer, Klemens Rumpf and Heinz Krenn; Institute of Experimental Physics, University of Graz, Graz, Austria.

To form a skeleton-template for a nanoscopic ferromagnetic needle array, a silicon wafer of appropriate doping (n-type, 0.01 Ohm cm) is anodized in an aqueous hydrofluoric acid electrolyte. If proper etching parameters ($j = 100\text{ mA/cm}^2$, HF 10%, bath temperature 20 degrees Celsius) are chosen, the pore growth can be controlled to form highly oriented channels perpendicular to the wafer surface. This is in contrast to luminescent porous silicon of spongelike nanoporous structure which is usually formed during electrochemical etching of crystalline silicon. Uniaxially oriented pores of meso-size ($> 10\text{ nm}$) can be prepared with, for instance, monodisperse pore diameters of about 60 nm and a length between 10 micrometer and 30 micrometer, depending on the etching duration. For doping densities above 10^{18} cm^{-3} the growth mechanism of pores is controlled by charge transfer due to band-to-band tunneling of carriers across the space charge

region. The porous layer is of good homogeneity and shows an abrupt termination to crystalline silicon. Apart from the well-defined diameter of pores also the two-dimensional spatial arrangement is in quasi-registry to the (001) silicon surface: It shows a square-like periodicity along the [100]- and [010] wafer surface directions, which is in contrast to the hexagonal ordering of arrays derived from alumina templates. The porosity is 50% and observations by high-resolution scanning electron microscopy show a density of 1.8×10^8 pores/mm². In a second electroplating process this self-assembled array of mesopores is filled with metallic Ni. The Ni-filling of the pores is between 1.2×10^{-5} g/mm² and 1.2×10^{-4} g/mm² of depths of 30 micrometer, depending on the Ni loading mechanism. The samples are imaged on the flat surface and on the cleavage edge by high resolution scanning electron microscopy, energy dispersive x-ray scattering, scanning Auger electron spectroscopy and magnetic force microscopy. The magnetic and magneto-optic properties of the nano-arrays of filaments are investigated by SQUID magnetometry and by magneto-optical (Faraday- and Kerr-) effect, respectively. The samples exhibit a tendency to perpendicular magnetic anisotropy due to the high aspect ratio (1:1000) of the Ni wires and show a two-mode switching (at $B = 0.05$ T and $B = 5.2$ T) in the hysteresis branches. The second steep ascent in the magnetization curve at 5.2 T could be important for an application as a silicon-based magnetic field sensor of high responsiveness.

R8.10

Fabrication of Periodic Mesostuctured Oxide Composites for Chemo-Optical Sensors. Sungyeon Choi¹, Marc Mamak¹, Georg von Freymann¹, Naveen Chopra² and Geoffrey A. Ozin¹; ¹Chemistry, University of Toronto, Toronto, Ontario, Canada; ²Xerox Research Centre of Canada, Toronto, Ontario, Canada.

With increased interest for the detection of various liquid and gaseous species in the environment, the demand for compact, low-cost, and real-time sensors has grown. The use of optical devices as chemical sensors is one of the best solutions for this demand since these types of sensors provide several advantages, such as high sensitivity without electromagnetic interference and remote sensing in harsh environments. Although several types of integrated chemo-optical sensors have been investigated, there is no example using periodic mesostructured oxide as a main material. Herein, the fabrication process of the first chemo-optical sensor based on a periodic mesostructured oxide composite will be presented with a demonstration of sensor sensitivity.

R8.11

SiC Supported VPO Catalyst for the Partial Oxidation of n-butane to Maleic Anhydride. Ala'a Kababji and John T. Wolan; Chemical Engineering, USF, Tampa, Florida.

A catalyst formula consisting of vanadium phosphorous oxide (VPO) supported on $2\mu\text{m}$ single crystalline α -SiC particles was formulated and tested for potential use in the partial oxidation reaction of n-butane to Maleic Anhydride. Different commercial SiC powder samples were also used to investigate the intrinsic catalytic selectivity of SiC to produce Maleic Anhydride in this highly complex exothermic reaction. The high thermal conductivity, high surface area and chemical resistance to attrition makes SiC a good choice for this application. A fixed-bed catalytic reactor was loaded with modified VPO formulas and in-situ FTIR was used to analyze the effluent stream products. The weight percentage loading of α -SiC in the VPO ranged from 6-90 wt%. The new supported catalyst formula lowered the reaction temperature from 420C to 400C, improved the catalyst activity and lifetime by helping dissipate the exothermic heat of the reaction, which resulted in 29% overall butane conversion to products, but lowered the overall yield and selectivity to Maleic Anhydride. The best loading range of α -SiC in VPO was found to be 10-50 wt%. Pd was used to promote the catalyst, and a catalyst system consisting of 1.5 wt% Pd/VPO supported on 10 wt% $2\mu\text{m}$ size α -SiC particles raised the actual yield to 25.3% up from 7.2% using VPO only.

R8.12

Facile Fabrication and Integration of Patterned Nanostructured Titania into Microsystems: Effect of Parent Ti Microstructure on Kinetics of Reaction. Diana DeRosa^{1,3}, Zuruzi Abu Samah^{1,2} and Noel MacDonald^{1,2}; ¹Materials Department, University of California, Santa Barbara, California; ²Mechanical and Environmental Engineering Department, University of California, Santa Barbara, California; ³Biosystems Engineering and Biochemistry and Molecular Biophysics Department, The University of Arizona, Tucson, Arizona.

Nano-structured titania (NST) has many desirable properties for integration into biological systems and nano/micro electrical mechanical systems (N/MEMS). NST is being considered for applications ranging from catalyst for organic decontamination, cell scaffolds for implantable devices and sensing elements for detection of

gases and biological macromolecules. One promising route for implementing ns-titania into N/MEMS devices is by reacting titanium films with aqueous hydrogen peroxide (H₂O₂) solution. Hence the effect of parent Ti microstructure and H₂O₂ solution on the morphology of NST produced needs to be understood. In this work we use an electro-oxidation method to probe the kinetics of the above reaction. We have investigated the effect of parent Ti film thickness, deposition rate of Ti films, H₂O₂ concentration and temperature on the reaction kinetics. We found two reaction kinetics depending on thickness of the parent Ti film. For films less than ~50 nm thick, the kinetics is interface-reaction controlled. For thicker films, the reaction is controlled by diffusion through an intermediate gel layer formed during the reaction. The titania gel layer has a porous sponge-like morphology and is amorphous. Upon annealing at 300 °C, the gel crystallizes into anatase nano-crystals about 5-25 nm diameter. We have used a variety of techniques to investigate the NST layer formed including UV-Vis, XRD, AFM, SEM and TEM.

R8.13

Study on the Control of the Titanate Nanotube Structure. Seong Youn Jeong and Hwan Kim; Seoul National University, Seoul, South Korea.

Various sized titanium oxide powders were prepared by hydrolysis of Titanium(IV) butoxide and using this powders we synthesized nanotube-shaped titanates (H₂Ti₃O₇) having various morphology. Normal spherical powders (raw materials) having various morphology was synthesized via the alkoxide sol-gel procedure. These powders were adopted as a starting material in preparing nanotube-shaped titanates. By controlling the amounts of HCl and NH₄OH catalysts added to water and the calcinations temperature raw materials having various crystallite sizes (15, 20, 25nm), particle sizes (50, 100, 200nm) and surface areas (30, 50, 100 m²/g) were prepared. Nanotube-shaped titanate was synthesized by a hydrothermal treatment. Raw materials mentioned in the above paragraph were immersed in a 10 mol NaOH solution at 150°C for 12h. The longer nanotubes were obtained by increasing the crystallite size and particle size. The particles were observed with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and XRD, respectively. The influence of crystallite sizes, surface areas and particle sizes on the formation of the titanate nanotube was investigated. And we confirm the formation mechanism that the sheet-like particles were believed to roll into nanotubes. Besides ascertained that the TiO₂ is not fully dissolved into NaOH solution and the formation of two dimensional sheet-like layered plate was partially dependent on the morphology of the raw material.

R8.14

Characterization of Noble Metal Nanocluster. Galif Kutluk¹, Shinya Yagi², Hiroshuke Sumida³, Hirofumi Namatame⁴ and Masaki Taniguchi⁴; ¹Innovation Plaza, Hiroshima, Japan Science and Technology Agency, Higashi-Hiroshima, Japan; ²Nagoya University, Nagoya, Japan; ³Mazda Motor Co., Hiroshima, Japan; ⁴Hiroshima University, Higashi-Hiroshima, Japan.

Noble metal represent the key component of three way catalyst as the catalytic activity occurs at the noble metal centre. The effect of metal particle size on catalytic properties has received considerable attention because the size of metal particle plays an important role in catalytic behavior. We have studied noble metal Pt, Pd and Rh nanocluster by Near Edge X-ray Absorption Fine Structure (NEXAFS) and X-ray Photoelectron Spectroscopy (XPS). The nanoclusters are deposited onto substrates (Si<100> and Ta thin films) by Gas condensation method, and the size of the cluster in diameter is controlled from 2nm to 10nm. The size of nanocluster on Si and Ta surfaces is characterized by combining with scanning electron microscope (SEM), atomic force microscopy (AFM) and transmission electron microscope (TEM). The size distribution is obtained by evaluating the well-dispersed clusters of numbers more than 300 from the TEM images under different experimental conditions. The quantum size effect of Pd nanocluster has been observed by L3-edge NEXAFS and XPS studies. It is found that the effect depends on the nanocluster size and the dispersion density.

R8.15

Highly Oriented Plate-Like Nanorods Arrays of ZnO. Ying Dai¹, Yan Jin Li², Xin Mei Pei¹ and Long Qiang Zhou¹; ¹School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China; ²Administration of Science and Technology, Wuhan University of Technology, Wuhan, Hubei 430070, China.

Highly oriented plate-like nanorods arrays of ZnO are synthesized by solution-based approach at low temperature. ZnO nanorod arrays grow oriented vertically on the silicon substrate and the nanorod consists of the pile of platelike ZnO single-crystal along the c-axis direction. The construction of platelike arrays is achieved by varying

the growth conditions. The growth mechanism is analyzed by XRD, SED, TEM and HRTEM based on the nuclear and growth process of ZnO. Photocatalytic properties of the nanostructures arrays are investigated. The novel ZnO nanorod arrays are expected to have great potential for sensing, catalysis and optical emission.

R8.16

Abstract Withdrawn

R8.17

Transferred to R5.1

R8.18

Synthesis of Dendrimer-Encapsulated Metal Oxide Nanoparticles in Supercritical Carbon Dioxide.

Robert L. Paddock, Venkateswarlu Juttukonda, Jason K. Vohs and Bradley Dean Fahlman; Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan.

There is currently a great deal of interest in the controlled synthesis of monodisperse metal oxide nanoparticles, for potential applications in gas sensors, microelectronics, and catalysis. Herein, we present the synthesis of WO₂, SnO₂, and TiO₂ nanoparticles utilizing a variety of poly(amidoamine) (PAMAM) and poly(propyleneimine) (PPI) dendrimers as templates to control the size and stability of the entrained species. Metallate ions (tungstate, stannate, and titanate) were combined with the dendrimers and reduced in a supercritical carbon dioxide environment. In our system, sc-CO₂ acts as both the reaction medium and the reducing agent, yielding the desired dendrimer-encapsulated metal oxide nanoparticles. A variety of characterization techniques such as UV-Vis spectroscopy, FESEM, X-ray diffraction, and HRTEM/EELS were used to assess the composition/structure of the dendrimer/metal oxide nanoparticles.

R8.19

Photo-Reactive Organic Semiconductor Nano Particles.

Tzung-Fang Guo¹, Jien-Wei Lu² and Thou-Jen Whang²; ¹Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan, Taiwan; ²Department of Chemistry, National Cheng Kung University, Tainan, Taiwan.

We report the fabrication of organic semiconductor nano-particles (OSNPs) based on the mini-emulsion of conjugated polymers. The colloids composed of polyfluorene co-polymers with electron acceptor material were stabilized by the surfactant and dispersed homogeneously at the aqueous solution. Under the illumination, the photoluminescence of OSNPs was quenched due to the ultra fast electron transfer from the excitons on the polymer chains to the electron acceptors. Highly reactive free radicals, such as super oxide anions and hydroxy radicals, were generated at the excited OSNPs by the separated electrons and holes, respectively. They function as a block agent to inhibit the duplication of DNA for virus or to react with the nearby organisms. The colloid particles can be transferred to the testing substrates or used directly in the aqueous solution.

R8.20

Template Preparation of Multi-segment Pt and Pt/Ru Nanorods as DMFC Anode Electrocatalysts in Acid Electrolytes. Fang Liu¹, Jim Yang Lee^{1,2} and Weijiang Zhou¹;

¹Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore; ²Singapore-MIT Alliance, Singapore, Singapore.

Cylindrical rods with uniform diameters on the nanometer scale can be obtained by electrodeposition of the target materials into anodic aluminum oxide membranes. This technique has been used to fabricate a variety of nanostructured materials. The most notable advantage of electrodeposition is the ability to sequentially deposit different materials in the templates yielding segmented nanorods. These multi-segment nanorods have found interesting applications in biology, magnetics, surface functionalization, and can offer unique opportunity in controlling the microstructure, and the geometrical and electronic properties of bimetallic catalysts for direct methanol fuel cells (DMFC) not obtainable with conventional preparation methods such as co-impregnation, co-precipitation, and microemulsion techniques. The present study is therefore aimed at producing structurally and geometrically controllable nanostructured DMFC electrocatalysts by the template electrodeposition method. Platinum and ruthenium are used as the catalyzing metals based on their demonstrated outstanding catalytic properties in methanol oxidation reactions. Pt and differently segmented Pt-Ru nanorods (Pt-Ru, Pt-Ru-Pt, Pt-Ru-Pt-Ru, Pt-Ru-Pt-Ru-Pt, Pt-Ru-Pt-Ru-Pt-Ru) were synthesized by electrodeposition into nanoporous alumina templates. Field emission scanning electron microscopy (FESEM) showed that the nanorods are about 200nm in diameters, 1.2 μ m in total lengths with 900nm of total Pt segment lengths. The alternating Pt and Ru segments could be differentiated as bright and dark regions

respectively in the micrograph because of the atomic weight difference. The presence of Pt(0), Pt(II), Pt(IV), Ru(0), Ru(VI) on the surface of the bimetallic nanorods was inferred from X-ray photoelectron spectra (XPS) measurements. X-ray diffraction (XRD) patterns of the PtRu nanorods indicated that Pt and Ru are polycrystalline with face-centered cubic and hexagonal close-packed lattice structures respectively. The Pt and segmented Pt-Ru nanorods were dispersed on a finely-polished glassy carbon electrode, and used as catalysts in the room temperature electrooxidation of methanol in acid electrolytes (0.1M HClO₄ and 0.5M CH₃OH). Cyclic voltammetry at 50mV s⁻¹ showed that for the same amount of Pt, the peak current densities increased with the increasing Pt-Ru pair sites concentration, which is proportional to the number of Pt-Ru interfaces. The relative rates of reaction as recorded by chronoamperometry showed a linear relationship between the long time (near steady state) current density and the number of Pt-Ru interfaces. The use of segmented nanorods with adjustable Pt-Ru interfaces removes many of the ambiguities in the interpretation of experimental data from conventional alloy catalysts, enabling a direct demonstration of the bifunctional mechanism and the establishment of a quantitative relationship between the number of pair sites and the catalytic activity in methanol electrooxidation.

R8.21

Clays Pillared by Zirconia Nanoparticles: Specificity of Structure and Adsorption Properties as Related to Catalysis of NOx Selective Reduction by Hydrocarbons in the Excess of Oxygen. Vladislav A. Sadykov¹, Tatyana G. Kuznetsova¹, Rimma V.

Bunina¹, Natalia V. Mezentseva¹, Dmitrii Efremov¹, Vasilii Avdeev¹, Vladimir P. Doronin¹, Vladimir L. Kuznetsov¹, Valerii A. Matyshak², Valerii V. Lunin³ and Aleksandr M. Volodin²; ¹Heterog. Catalysis, Borekov Inst. of Catalysis, Novosibirsk, Russian Federation; ²Semenov Inst. of Chem. Phys., Moscow, Russian Federation; ³Chem. Dep. of Lomonosov Moscow State Univ., Moscow, Russian Federation.

Grand Canonical Monte Carlo (GCMC) simulation was applied for analysis of the low-temperature nitrogen adsorption in the micropores of a montmorillonite clay pillared with zirconium polyoxocations synthesized via aging of zirconyl chloride solutions containing Ca, Ba or Sr cations. All samples possess developed microporosity (gallery height up to 1nm) and mesoporosity (pore sizes up to 5 nm), the latter being formed due to defects in clay sheets stacking. While sheet-like Zr₈ complexes dominate for the case of samples prepared with Sr-containing solutions, only isolated tetramers Zr₄ appear to exist in the interlayer micropores of samples pillared with Ba- or Ca-containing solutions. Modeling by DFT and semiempirical PM3 method revealed that in solution, sheet-like species are favored by energy thus being preserved after pillaring, washing and calcination of samples. Less stable rod-like zirconium polyoxocations stabilized by Ca and Ba cations dissipate into separate tetramers after entering into the clay interlayer space due to a strong interaction with aluminosilicate layers and washing out of alkaline-earth cations. This specificity of nanopillars structure is reflected in a high density of bridging hydroxyls and a low density of Lewis acid sites - coordinatively unsaturated Zr⁴⁺ cations as revealed by FTIRS. Existence of terminal hydroxyls bound with Zr cations was revealed by their ability to exchange for EPR detected superoxide O₂⁻ species by treatment with liquid H₂O₂ at room temperature. Catalytic properties of these systems loaded with Cu cations and promoted by Pt were characterized in the reactions of NOx selective reduction by propylene and decane in the excess of oxygen. Supported Cu cations and Pt strongly interact with bridging hydroxyls of nanosized pillars and with each other which ensures an optimum oxygen bonding strength preventing undesirable combustion of hydrocarbons, while accelerating activation of reagents. The details of the reaction mechanism were elucidated using pulse titration experiments and in situ FTIRS studies of intermediates transformation. Nitrate and nitroorganic complexes were shown to be key intermediates participating in rate-determining steps, their composition, structure and reactivity being dependent upon the specificity of Zr nanoparticle structure. Catalytic performance of best samples in the NOx selective reduction by hydrocarbons in the low-temperature (200-300 oC) region is comparable with or higher than that of systems based upon ZSM-5 while being stable in the presence of water and sulfur dioxide. Sulfation even helps to improve performance of Cu+Pt-loaded Zr-pillared clays due to decreasing bonding strength of nitrates and favoring hydrocarbons transformation into oxygenates. This work is in part supported by Integration Project 8.17 of Presidium RAS.

R8.22

Homogeneous Catalysts Tethered to Carbon Nanotubes.

Leonard S. Fife¹, John C. Linehan¹, R. Shane Addleman¹, Christopher L. Aardahl¹, J. David Newell² and Thomas E. Bitterwolf²; ¹Pacific Northwest National Laboratory, Richland, Washington; ²University of Idaho, Moscow, Idaho.

Carbon nanotubes present an attractive option for use as a solid

support on which to tether homogeneous catalysts. There are a growing number of methods available to chemically modify the large accessible surface of carbon nanotubes. Additionally, carbon nanotubes may be grown or incorporated into hierarchically ordered, multi scale structures to optimize catalyst performance, maximize the number of active sites in a given volume of material, and to facilitate incorporation of the catalyst material into macro scale systems and devices. A model system consisting of a Rhodium center with a 1-(amino) methyl pyrene ligand anchored onto multi walled carbon nanotubes was used to investigate the activity, selectivity, and stability of organometallic homogeneous catalysts noncovalently tethered to carbon nanotubes. Material synthetic methods and promising catalytic activity results for the hydroformylation of 1-octene based on this system will be presented.

R8.23

Patterning Ion-Channel Functionality in Supported Membranes Using Topochemically Patterned Sol-Gel Silica Supports. Calvin Yang^{1,2}, Chanel K. Yee² and Atul N. Parikh²;

¹Biomedical Engineering, UC Davis, Davis, California; ²Dept. of Applied Science, UC Davis, Davis, California.

We present a new material construct directly coupling a topochemically patterned silica substrate as an optically-amplified signal transducer with an ion-channel incorporating phospholipid bilayer as a biomimetic recognition element toward the development of a general biosensing principle. Specifically, we prepared geometrically defined patterns of sol-gel silica films displaying (1) hydrophobized regions of mesostructure (MS) that were also functionalized in the bulk of the film using a pH sensitive FITC dye and (2) hydrophilic regions comprising nanoporous silica mesophase (MP). MP patches were spatially created within the silanized MS film by the selective removal of all organic moieties using deep UV irradiation and a photomask, forming water-filled nanoscale pores in the exposed regions by adapting a previously reported method. Spreading of gramicidin containing phospholipid vesicles onto such a surface resulted in single lipid monolayers on hydrophobic MS regions whereas full bilayers formed on the hydrophilic MP regions of the sample. The lipid monolayers on the MS regions precludes the assembly of functional gramicidin dimers. By contrast, full single bilayers on the MP regions of the sample facilitate the assembly of the functional gramicidin dimer within the membrane phase. Fluorescence intensity of the FITC-doped MS film was monitored as proton transport was facilitated by simply changing the pH of the ambient medium. Our data establish unambiguously that bilayer regions of the sample show easily measurable changes in the fluorescence intensities as a function of pH whereas lipid monolayers on the MS regions of the sample remain unaffected. Control experiments using homogeneous lipid vesicles reveal no such pH dependent variations in the fluorescence intensity ratios. We expect this model to provide a generic biosensing mechanism for applications in the detection of a broad class of neurotransmitters (e.g. glutamate, GABA or dopamine) and monitoring their concentration variation in real time. We are currently exploring these applications. This work was supported in part by the NSF Center for Biophotonics Science and Technology and a grant from Basic Energy Sciences, Office of Science, U.S. Department of Energy.

R8.24

Preparation of a Supported Si₃N₄ Membrane for Gas Separation. Fei Cheng¹, Stephen M. Kelly¹, Stephen Clark¹, John S. Bradley¹, Marc Baumbach² and Andreas Schutze²; ¹Chemistry, University of Hull, Hull, United Kingdom; ²Lab for Measurement Technology, Saarland University, Saarbrücken, Germany.

Due to their chemical and thermal stabilities, porous ceramic membranes are highly promising for use in current separation technology, particularly at high temperatures and in chemically harsh conditions. In our group, we have developed a non-oxide sol-gel method for the preparation of high-surface-area mesoporous silicon nitride powder. ¹ In this work, we report the preparation of a novel supported Si₃N₄ membrane via this non-oxide sol-gel process and its gas separation properties as part of the NANOSENSOFLEX program. The supported Si₃N₄ membrane was prepared by the sol-casting process, in which an α -Al₂O₃ macroporous support was put in contact with a silicon diimide sol prepared by acid-catalyzed ammonolysis of tris(dimethylamino)silylamine H₂NSi(NMe₂)₃.¹ After drying at room temperature under N₂ flow overnight the sample was pyrolyzed at 1000 °C for 2 h. The interaction of the membrane with CO, NO₂, H₂, and propane was evaluated on a computer-controlled gas test bench using broad-band sensors. The SEM images indicated the presence of a Si₃N₄ membrane with thickness about 2.3 μm on the surface of the α -Al₂O₃ support. Since the α -Al₂O₃ disk is macroporous and the silicon diimide sol will penetrate the pores of the disk during the dipping, Si₃N₄ membranes on the surfaces of the pores are also observed. Nitrogen adsorption analysis indicated that although most of the pores were similar to those of an α -Al₂O₃ disk,

a new pore size distribution at 2-5 nm, similar to that for Si₃N₄ powder,¹ was observed. The new membranes demonstrate high selective absorption of NO₂. The separation factors of N₂ to CO, H₂ and C₃H₈ are 3.3, 7.5 and 2.5 respectively, suggesting a potential application as a selective filter for gas sensors.¹ F. Cheng., S. Clark, S. M. Kelly, J. S. Bradley and F. Lefebvre, J. Am. Ceram. Soc., 2004, 87, 1

R8.25

Sol-gel Derived Aminosilicate Nanoporous Molecular Sieve Membrane for CO₂/Air Separations. George Xomeritakis¹, Andy Tsai^{2,1} and Jeffrey Brinker^{3,1}; ¹Center for Microengineered Materials, The University of New Mexico, Albuquerque, New Mexico; ²T3 Scientific LLC, Arden Hills, Minnesota; ³Sandia National Laboratories, Albuquerque, Minnesota.

Nanoporous inorganic molecular sieve membranes are gaining increasing attention for high-temperature size- and/or adsorption-based selective gas separations, e.g. H₂/N₂, CO₂/(CH₄ or air) and isomers. Among the various types of inorganic membranes, sol-gel silica nanoporous membranes offer good potential for future commercialization, because they combine a number of advantages including high processibility, tunable pore size and narrow pore size distribution, and tailored chemical functionality. One of the most significant challenges for inorganic molecular sieve membranes is the separation of permanent gases with difference in kinetic diameter smaller than 0.2 Å, e.g. O₂/N₂ or CO₂/(CH₄ or Air). For such demanding separations, crystalline molecular sieves such as zeolites appear promising candidates, but their preparation in membrane form with minimal non-selective inter-zeolitic porosity remains an elusive task. On the other hand, amorphous nanoporous molecular sieves such as sol-gel silica or pyrolytic carbon are characterized by pore size distributions wider than those of zeolites, and hence cannot offer high selectivities for such demanding separations. However, if additional adsorption-based selectivity, combined with size-based selectivity, is introduced to an amorphous molecular sieve, it is possible to enhance its selectivity intrinsically, due to specific interactions of the adsorbent material with one gas permeant, and subsequent blocking of diffusion of non-adsorbing mixture components. In order to demonstrate this concept of dual-functional molecular sieve membrane, we prepared a new type of nanoporous silica membranes with amine functional groups incorporated in the inorganic silica matrix, for the purpose of enhancing the CO₂ selectivity of the membrane over O₂ and N₂, in the presence of water vapor. Such a membrane that can selectively permeate CO₂ from humid air has potential application in removal of metabolic CO₂ from breathing air loop or CO₂ capture from power plant emissions. We have followed 2 approaches in order to introduce the amine groups in a standard silica membrane, for enhanced CO₂ activity. In the first approach, we have used an aqueous amine salt solution/silica sol mixing method in order to physically immobilize the amine groups inside the inorganic silica matrix. In the second approach, we introduce amine groups covalently bonded on the inorganic silica matrix. Both approaches required significant modification of the previously established sol-gel recipes for the synthesis of purely siliceous silica membranes. In the proposed presentation, we will describe the concept of the novel, dual-functional aminosilicate molecular sieve membrane for CO₂/Air separation and present comprehensive single-component and multicomponent gas permeation results in order to understand the transport mechanism of these membranes and assess the effectiveness of the new approach for enhancing membrane selectivity.

R8.26

Transferred to R10.2

R8.27

Characterization of Nanoporous Materials Prepared from Montmorillonite Clay and its Application to the Decolorization of Mare's Milk Oil. Temuujin Jadambaa¹,

Mamoru Senna¹, Jadambaa Tsedev², Burmaa Dashdendev², Erdenechimeg Shaarii² and Amarsanaa Jadambaa²; ¹Faculty of Science and Technology, Keio University, Yokohama, Kanagawa, Japan; ²New Materials Center, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia.

Nanoporous materials have been prepared by leaching the purified montmorillonite clay with sulfuric acid (H₂SO₄) solution with varying concentrations (0.5-2M) at 80°C for 0.5-4h. Acid leaching causes partial amorphisation of the clay with depletion of MgO, Al₂O₃, Na₂O and Fe₂O₃ components mostly from interlayer and octahedral sites. This increases the specific surface area by more than 3 times, i.e. from 49.1 to 157m²/g. Surface acidity of the original montmorillonite increases from 13.7 (mequiv/100g sample) to the highest value, 73.4 (mequiv/100g sample) in the sample leached with 0.5M H₂SO₄ for 4h. The TEM and pore-size distribution curves calculated from the desorption isotherms of the leached montmorillonite show that most

of the pores are in mesoporous region with their diameter of 3-4nm. This material turns out to be appropriate for bleaching of the mare's milk oil. The bleaching efficiency of the porous materials judged by relative light absorbance of the oil at 400nm increases from 9.5% to 93.8% in clay leached by 2M H₂SO₄ for 4h. Increased surface acidity is mainly responsible for better adsorption of coloring pigments. There is a linear dependence of the bleaching efficiency on the surface acidity and specific surface area. Acidity number depends on the amount of the cations removed both from interlayer and octahedral area, which in turn is influenced by the acid concentration. At lower acid concentration, there is linear relationship between the acidity and the surface areas. However, with increasing acid concentrations over removal of the octahedral cations occurs with decreasing the acidity, but increasing the specific surface area. These chemical and structural changes are discussed in terms of the decolorization capacity.

R8.28

Abstract Withdrawn

R8.29

Thin Film Deposition on Opal Matrix. Yury Panfilov¹ and Michail Samoilovich²; ¹MT-11, Moscow State Bauman University of Technology, Moscow, Russian Federation; ²Photonics, Technomash, Moscow, Russian Federation.

Opal matrix represents close-packed (primarily, according to the cubic low) silica nanospheres (very close to each other in diameter) whose sizes may vary from 200 to 600 nm for different samples. With the spherical diameter specified, these packings contain structural voids, 180-400 nm in size, which may be partially or totally filled with semiconductors, superconductors, optically amplified, magnetic and other materials. Vacuum coater with three types of source (DC magnetron sputtering system, ion-beam source, arc evaporator) was elaborated for thin film deposition on opal matrix. Multilayer thin film coating with Ti and DLC (diamond like carbon) layers for field emission application was deposited by means this coater. Millimeter-thick opal matrix plates containing diamond grains of size 2-5 nm (preserved as nucleating centers upon diamond growth) and carbon were imbedded in opal plates by the ion-plasma method. Magnetic Ni coating on opal matrix was deposited by vacuum thermo-ion and liquid electro-deposition methods. The photoluminescence nanocomposite, in which erbium oxide was introduced into interstitial voids of opal matrix, was formed by the methods of impregnation and sol-gel. The thermo-CVD procedure for embedding silicon in opal pores resulted in a sample, in which the sublattice of voids was 100% filled with silicon. The composite opal-Si and inverted opal were examined by X-ray structural phase analysis, Raman scattering spectroscopy, transmission and scanning electron microscope. Also synthesized in the opal matrix was a three-dimensional lattice of the clusters GaAs (45-50 nm).

R8.30

New Open-Framework Materials. Xianhui Bu, Cal. State Univ. Long Beach, Riverside, California.

Syntheses and structures of some new open-framework materials with novel framework compositions and unique topological features will be presented. These materials are prepared by controlled variation of synthetic parameters in hydrothermal systems. A variety of chemical compositions have been explored, including either main group or transition metals.

R8.31

Fabrication of Anodic Alumina Film with Custom-designed Arrays of Nanochannels. Nai-Wei Liu^{1,2}, Anindya Datta¹, Chih-Yi Liu¹, Huai-Hsien Wang³, Cheng-Yi Peng³ and Yuh-Lin Wang^{1,3}; ¹Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; ²Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; ³Physics, National Taiwan University, Taipei, Taiwan.

Among the strategies for growing one-dimensional straight nanostructure such as nanorods and nanowires, a viable approach is to grow the materials into templates with aligned nanochannels. Recently, porous anodic aluminum oxide (AAO) film has become an attractive template material for its self-aligned array of nanochannels. For certain applications of AAO, it is desirable to isolate to create an array with specific number of nanochannels arranged in a desired geometry. This objective is not easily achievable due to the high density of a typical nanochannel array on AAO. In this work, we have demonstrated, for the first time, a focused ion beam (FIB) direct-write lithographic method for selectively closing part of the channels of an ordered array on an AAO film creates a custom-designed nanochannels array. The initial ordered arrays are fabricated by FIB lithographic guiding techniques while the closure of the nanochannels within certain area is achieved by FIB bombardment of the AAO film. The successful fabrication of such a template with custom-designed nanochannel arrays opens up numerous possibilities for the creation of

nanowire arrays with desired geometry.

R8.32

Silver-filled Porous Anodic Alumina Substrate with Uniform and Ultrahigh Raman-Signal Enhancing Factor. Huai-Hsien Wang¹, Chih-Yi Liu², Shr-Bin Wu³, Cheng-Yi Peng¹, Nai-Wei Liu^{2,4}, Juen-Kai Wang^{2,5} and Yuh-Lin Wang^{1,2}; ¹physics, National Taiwan University, Taipei, Taiwan; ²Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; ³Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei, Taiwan; ⁴Materials Science and Engineering, National Taiwan University, Taipei, Taiwan; ⁵Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

In this contribution, we report uniform surface-enhanced Raman scattering (SERS) enhancement by silver nanoparticles in anodic alumina channels. Silver nanoparticles are electrochemically deposited into arrays of anodic alumina channels with uniform inter-channel spacing between 30 and 100 nm. The substrates exhibit spatially uniform Raman scattering enhancers, which are in great contrast to existing SERS substrates. Our study shows that the largest Raman enhancement factor of rhodamine 6G is ten order and the factor decreases with increasing gap between silver nanoparticles. These substrates are thus potentially useful in the application of SERS to biological analysis in which repeatability and sensitivity are two key issues.

R8.33

Growth and Characterization of Iron Silicide Nanowires on Si(110). Shengde Liang, Rafiqul Islam, Zhian He, David Smith and Peter Bennett; Arizona State University, Tempe, Arizona.

Iron silicide can be metallic, magnetic, and semiconducting, depending on the growth condition. In this paper, we report the growth of epitaxial iron silicide nanowires by PVD in UHV on Si(110) substrate at 700 degree C. Nanowire dimensions are very uniform from images of Tapping mode AFM: height, width and length are 5nm, 10nm and 4micrometer respectively. From the HRTEM images, It was found that the silicide nanowires are metastable cubic phase, r-FeSi₂ with epitaxial relationship : r-FeSi₂(111)//Si(111), r-FeSi₂<110>//Si<110>. Magnetic properties by holography is on progress. In-situ annealing at 720 degree C of these samples for 1.5hrs causes phase transformation: cubic r-FeSi₂ to orthorhombic beta-FeSi₂, with epitaxial relationship:beta-FeSi₂(101)//si(111) and FeSi₂<010>//Si<110>, which has a lattice mismatch of -1.29% along Si<110> and 5.5% along Si<112>. This phase is semiconducting with direct band gap of 0.87eV.

R8.34

Molecular Squares: Ground State Electronic Structure and Conformational Properties. Donald E. Ellis^{1,2}, Ljubomir Miljacic¹, Bin Deng², Ming Jiang⁵, Lev Sarkisov⁴ and Randall Snurr³; ¹Physics and Astronomy, Northwestern University, Evanston, Illinois; ²Chemistry, Northwestern University, Evanston, Illinois; ³Chemical Engineering, Northwestern University, Evanston, Illinois; ⁴Chemical Engineering, Yale University, New Haven, Connecticut; ⁵Physics, Yantai University, Yantai, China.

Rectangular macromolecules built up from [ReCl(CO)₃R₂] "cornerposts" with linking macrocycle "walls" self-assemble into thin film and crystalline structures with distinctive porosity. They have been shown to be useful in selective guest-host chemistry, size-selective transport, chemical catalysis and sensing. Some of them serve as a prototype for a structurally constrained catalytic system. We present theoretical analyses of electronic structure of several of the squares and related fragments. Using the first-principles Density Functional approach we derive electronic charge distributions that reveal bonding structure and spectral distributions. We show that the analysis of conformational preferences can be greatly simplified by using a "piecewise" strategy, which enables us to make a few generic statements about conformation of this class of macromolecules, and to offer design principles for controlling structure. To further illustrate advantages of this approach, we analyze the origin of (meta)stability of the planar conformation of the bipyridine square.

R8.35

Nanoporous TiO₂ Photoelectrodes on Patterned Substrate for Efficient Dye-Sensitized Solar Cells. Seok-Soon Kim, Jun-Ho Yum, Yong-Young Noh, Jang Jo and Dong-Yu Kim; Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

Dye-sensitized solar cell (DSSC) is a new type of photoelectrochemical solar cells composed of a dye-modified wide band gap semiconductor electrode, a counter electrode, and an electrolyte containing a redox couple. In spite of the cost-efficiency, permanence, and environmental compatibility of DSSC for practical applications, the improvement of

efficiency and long-term stability is inevitable. In general, the nanosized TiO₂ particles are used in the fabrication of photoelectrode to maximize the surface area of electrode that renders high amounts of adsorbed dye molecules and simultaneously highly efficient light harvesting. In addition, approximate 70 % improvement in device efficiency has been reported by the application of light-scattering particles or scattering layer on the nanosized TiO₂ porous electrode. To improve cell performance by increased optical path length of the incident light resulted from the multiple reflection or scattering, transparent conducting oxide substrate was patterned using a variety of techniques such as stamping, nanosphere lithography and so on. Additionally, Pt-TiO₂ counter electrodes prepared by the rf magnetron cosputtering system were applied to the cell fabrication due to the high active surface area and reflectance, resulting in the increase of photocurrent.

R8.36

Preparation of NiMoP/SiO₂ by Temperature-Programmed Reduction Procedure. Hee-Chul Woo¹, So-Yeon Lee¹ and S. Ted Oyama²; ¹Division of Applied Chemical Engineering, Pukyong National University, Pusan, South Korea; ²Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

More tight environmental regulations require the need to develop the better catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of petroleum feedstocks. Recently, a series of experimental results show that the transition metal phosphides display a substantial improvement for these reactions as compared to a commercial Co-Mo-S/Al₂O₃ catalyst. Most of these phosphide catalysts are monometallic phosphides such as Ni₂P, MoP, Fe₂P, WP and CoP. The supported monometallic phosphides for catalysis applications can be prepared at moderate temperatures by hydrogen reduction of dispersed phosphate phase on a solid support (typically silica or alumina) via conventional impregnation. However, few preparative methods have been explored for the supported bimetallic phosphides as active catalysts. The objective of the present study is therefore to synthesize silica-supported NiMoP through the combination of precipitation-deposition and impregnation and to investigate the effect of preparation conditions such as loadings, reduction rates, and phosphorous sources. For the oxidic precursor of NiMoP/SiO₂, silica was deposited through the co-precipitation reaction of an aqueous solution mixture of nickel nitrate and ammonium molybdate and then dried at 110 °C for overnight. After drying or calcining, the precursors were subsequently impregnation with an aqueous solution of ammonium hydrogen phosphate (AMP) or phosphoric acid (PAC), dried at 110 °C for overnight, and then calcined at 450 °C for 6h in air. Temperature-programmed reduction (TPR) has been used to gain qualitative information on the reducibility of oxidic precursors and the formation of NiMoP. The oxidic and reduction samples were characterized by XRD and FT-IR. Our results show the effect of phosphorous sources and Ni-Mo-P contents on the structure of samples. The TPR traces of mass 18 (H₂O) showed apparently the same profile regardless of phosphorous sources. For higher Ni-Mo-P contents, two reduction maximum peaks were shifted to higher temperatures with increasing of intensities. These trends are similar to those of silica-supported NiMoO₄, while the presence of P leads to a decreased reduction temperature. From the XRD results, AMP-impregnated samples have a single phase of crystalline NiMoP on silica. But in the PAC-impregnated samples, both the MoP and NiMoP phases are present. The formation of NiMoP phase on silica is particularly promoted at a below 5 °C/min of reduction rate. The reduction temperature of silica-supported oxidic precursor for NiMoP formation was 530-600 °C. In conclusion, the silica-supported NiMoP has been prepared, and the formation of NiMoP on silica strongly depends on the phosphorous sources as well as reduction rates, but not the content of Ni-Mo-P.

R8.37

Surface Stress-Charge Coefficient of Nanoporous Platinum in Dilute Electrolytes - Double-layer Processes versus Chemisorption. Raghavan Nadar Viswanath¹, Dominik Kramer¹ and Jorg Weissmuller^{1,2}; ¹Institut fuer Nanotechnologie, Forschungszentrum Karlsruhe, Karlsruhe, Germany; ²Technische Physik, Universitaet des Saarlandes, Saarbruecken, Germany.

The microscopic processes which control the dependency of the surface stress of the metal-electrolyte interface on the superficial charge density are the subject of debate. Specifically, this concerns the relative importance of changes of the surface bonding in the metal surface, as opposed to the formation of chemical bonds with adsorbed ions. Here, we report an experimental study of the variation of the surface stress with surface charge density for nanoporous Pt immersed in aqueous solutions of NaF of various concentration. As the concentration is reduced, we find initially an increase in the magnitude of the surface stress-charge coefficient, followed by saturation at a value of -1.9 V. Since specific adsorption is expected

to be reduced as the solution becomes more dilute, in favor of the capacitive charging, the results support the notion that changes in the bonding at the metal surface play a decisive role in determining the change in the surface stress during double-layer charging.

R8.38

An Analysis of the Structure of Lead Hydroxyvanadinite. Donald E. Ellis¹, Joice Terra², Jean Guillaume Eon³, Carlos Bauer Boechat⁴ and Alexandre Malta Rossi²; ¹Physics and Astronomy, Northwestern University, Evanston, Illinois; ²Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, Brazil; ³Instituto de Química, Univ. Federal de Rio de Janeiro, Rio de Janeiro, Brazil; ⁴Instituto de Química, Univ. Federal Fluminense, Niteroi, Brazil.

Hydroxyvanadinite, HVA, Pb₁₀(VO₄)₆(OH)₂ was prepared by a wet precipitation method and analyzed by X-ray absorption spectroscopy (XANES, EXAFS), Raman scattering and X-ray diffraction (XRD). The VO₄ tetrahedra were found to be strongly distorted, with three different values of vanadium oxygen distances (1.69, 1.72 and 1.75 Å). The XRD pattern was compatible with space group P6₃/m (176) and cell parameters a = 10.1938 Å and c = 7.4499 Å. The spectroscopic data were used in a Rietveld refinement of the XRD pattern; a crystallographic structure of the compound is proposed, in agreement with these data. The electronic structures of clusters representing the proposed HVA structure were investigated, employing the first-principles self-consistent discrete variational method and local-density theory. Mulliken atomic-orbital populations, densities of states and charge-density maps were obtained to study the Pb - O interaction and evaluate the influence of the lone-pair electrons of lead at the sixfold positions in determining the location of the OH ions and the chemical reactivity associated with Pb sites. The electronic structure of vanadinite, Pb₁₀(VO₄)₆Cl₂, was also investigated and used as a structural prototype. The utility of mixed vanadinite/ lead hydroxyvanadinite nanoparticles as low temperature oxidation catalysts is discussed.

R8.39

Effect of Surface Area of Carbon Source on the Carbothermal Reduction for ZnO Nanofabrication. Young Soo Lim¹, Seung-Tae Hong¹, Jonggeol Kim¹ and Jung Min Ko²; ¹Corporate R&D, LG Chem/Research Park, Daejeon, South Korea; ²Information & Electronic Materials R&D, LG Chem/Research Park, Daejeon, South Korea.

Due to its unbounded impacts and applications, there has been an explosive growth in nanoscale science and technology in last few years. Various nanostructures, such as nanotube, nanowire, nanobelt, nanoring, nanopin, and nanopropeller, have been synthesized and characterized. Among them, ZnO nanostructure has attracted much attention because of optoelectronic applications in blue or ultraviolet range due its wide band gap and large exciton binding energy. There are various methods for fabricating ZnO nanowire, but carbothermal reduction is known to be a relatively simple, cheap and suitable process for large scale production. Heating the mixture of ZnO and carbon powder up to a reaction temperature, ZnO(s) can be reduced by C(s) through solid-solid reaction, and the vaporized Zn(g) can be deposited as an oxide form on a catalyst-deposited substrate. As the carbon source for the carbothermal reduction process, graphite carbon has been generally used, that has a surface area(As) of ~10 m²/g. In this work, we have focused on the effect of surface area of carbon source to enhance the solid-solid reaction between ZnO(s) and C(s). Carbon black has a relatively large surface area of 30 ~ 1600 m²/g, so that there are more carbon atoms on the surface of the powders. Because the surface atoms can move more freely than bulk atoms, it is expected that Zn(g) would be more efficiently vaporized. ZnO nanostructure was prepared with a fixed amount of the mixture of high purity ZnO powder (0.2 g) and carbon powder (0.05 g). For a systematic comparison, graphite (As = 10 m²/g) and three kinds of carbon black powders (As = 30, 250, and 800 m²/g) were used as the carbon source. The mixture was loaded on a platinum boat, and then placed at the closed end of a quartz tube. Au-catalyzed Si as a substrate was also placed at the other region in the tube. The tube was inserted into a horizontal tube furnace. The platinum boat was heated in air up to 1050 oC with a heating rate of ~16 oC/min. After 30 minutes of heating, this process resulted in various products of ZnO nanostructures, such as nanowire, nanocomb, nanoflower, and nanomultipod, depending on the surface area of carbon source. The nanostructures were characterized with an x-ray diffractometer, a scanning electron microscope, and a high voltage transmission electron microscope. The formation mechanism of ZnO nanocomb structure will be discussed.

R8.40

Novel Synthesis of Hierarchical Porous Carbon Supports and their Application to Highly Efficient Electrode Materials for Fuel Cell. Jong-Sung Yu, Geun Seok Chai and Suk Bon Yoon; Chemistry, Hannam University, Daejeon, South Korea.

Fabrication of macrostructurally patterned highly ordered fully interconnected hierarchical porous carbons with uniform mesoporous walls has been demonstrated by template replication of aggregates of the small silica particles as molds, which were also templated by self-assembled ordered lattice of larger monodisperse polystyrene spheres. The size of the large macropores can be manipulated by controlling the diameter of the polystyrene spheres, while the size of the small mesopores and the overall specific surface area are determined by the silica particles. The mesopores can be easily regulated in the full mesopore range by proper size control of the silica particles. Due to unique structural properties of the porous carbon with fully interconnected ordered uniform bimodal porosity and high surface area, the carbon could work as an excellent catalyst support, resulting in great improvement for methanol oxidation activity in direct methanol fuel cell.

R8.41

Characterizations of Metal-Incorporated Carbon Aerogels Prepared Using Supercritical CO₂ Assisted Deposition and Structurally-Modified Derivatives. Dafei Kang¹, Ying Zhang²,

Carl D. Saquing², Can Erkey² and Mark Aindow¹; ¹Department of Materials Science and Engineering, University of Connecticut, Storrs, Connecticut; ²Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Carbon aerogels are novel mesoporous material with open pore structure the length scale of which can be adjusted at nanometer scale. Carbon aerogels have high specific surface area, low mass density, and high electrical conductivity, which makes them particularly well suitable for various applications ranging from electrodes (e.g. supercapacitors, fuel cells) to host material such as heterogeneous catalyst support for a wide selection of chemical processes. Carbon aerogels (CAs) with tailored pore properties were prepared via a procedure that involved a sol-gel process aided with the use of supercritical CO₂. Nanoparticles of selected metals (Ru, Pt) were supercritically incorporated into the porous CA network. An array of techniques was used to characterize both pure and metal-loaded CAs in an effort to investigate not only the structural characteristics of naked CAs but also the behaviors of metal particles when embedded in the carbon support. Structural modification of pure and metal-loaded CAs has also been developed. Results from high-resolution transmission electron microscopy (HRTEM) and other techniques confirmed that new structures were formed, which may be considered for applications fundamentally different from those proposed for pure and metal-loaded carbon aerogels.

R8.42

Abstract Withdrawn

R8.43

Optoelectronic Characteristics of Close-packed HgTe Nanoparticles in the Infrared Range. Hyunsuk Kim¹, Kyoungah

Cho¹, Byungjun Park¹, Jin-Hyoung Kim¹, Jun Woo Lee¹, Sangsig Kim¹, Taeyong Noh² and Eunjoon Jang²; ¹Electrical Engineering, Korea Univ., Seoul, South Korea; ²Samsung Advanced Institute of Technology, Suwon, South Korea.

Absorption, photoluminescence (PL), photoresponse, and I-V measurements were made for a close-packed HgTe nanoparticle film without organic capping materials to investigate its optoelectronic characteristics in the infrared (IR) range. In the absorption and PL spectra taken for the close-packed nanoparticle film, the wavelength of exciton peak was red-shifted, compared with 1-thioglycerol capped HgTe nanoparticles dispersed in solution. For the HgTe nanoparticle film, dark current was below several pA level, current was increased by about 3 orders of magnitude at a biased voltage of 3 V under the illumination of 1100nm wavelength light, and photoresponse was rapid with no current decay. This improvement originates from the removal of the capping material of 1-thioglycerol, resulting in the elimination of the electron charging effect; this has been thought to be the origin for the degradation of optoelectronic characteristics of nanoparticles such as current decay and slow photoresponse. These results illustrate that HgTe nanoparticles are one of promising materials for the photodetector in the IR range. Finally, the temperature dependence of the I-V curves is analyzed, and its origin is discussed.

R8.44

Transport Mechanism of Charge Carriers in 1-Thioglycerol-Capped CdTe Nanoparticles. Dong-Won Kim,

Jin-Hyoung Kim, Kyoungah Cho, Hyunsuk Kim, Byungjun Park and Sangsig Kim; Electrical Engineering, Korea Univ., Seoul, South Korea.

Photocurrent and dark current of 1-thioglycerol-capped CdTe nanoparticles were characterized to investigate transport mechanism of charge carriers in these nanoparticles. A film of the 1-thioglycerol-capped CdTe nanoparticles was coated on an ITO glass

substrate, and an Al contact was made on the top of this film. A significant dark current in the film without any applied voltage was observed. On the exposure of above-gap and below-gap light on the film, photocurrent responded rapidly and it decayed with the lapse of time. For the film with applied voltages, the intensities and decay curves of the dark current and photocurrent were strongly dependent on the polarity and strength of the applied voltages. These observations revealed that the charge carriers of the dark current are electrons, but that holes contribute dominantly to the photocurrent. Furthermore, they showed that electrons excited thermally or optically transport trap-mediatedly in the nanoparticles, and that holes excited optically transport in the extended bands of the nanoparticles.

R8.45

Novel Hybrid Composite for UV-Shielding. Shanghua Li¹,

Muhammet Toprak¹, Do Kyung Kim^{2,1} and Mamoun Muhammed¹; ¹Materials Science and Engineering, The Royal Institute of Technology, Stockholm, Sweden; ²Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Organic-inorganic hybrid materials with a polymer matrix have attracted considerable interest since they usually combine desirable properties from inorganic and polymer components[1,2]. Recently, incorporating nanosized particles into the polymer matrix opens new possibilities of achieving multifunctional materials. Nano-ZnO is one of the multifunctional inorganic nanoparticles that have drawn attention due to its many significant physical properties, such as chemical stability, high catalysis activity, low dielectric constant, and intensive UV and IR absorption etc. It has been used in many products such as fibers, plastics and cosmetics as UV resistant components[3]. The introduction of ZnO into polymers could improve the mechanical and optical properties of the polymer due to a strong interfacial interaction between the polymer and inorganic nanoparticles and nanoparticles small size and large specific surface area, and quantum effects respectively. In this work, PMMA-ZnO hybrid nanocomposite was first prepared by a sol-gel in-situ transition polymerization process. Structural and optical properties of the composite were investigated by transmission electron microscopy and ultraviolet-visible spectrophotometry. Transparent homogenous hybrid composites with different colours from yellow to brown were achieved by varying the composition of the sol. The low content of zinc (<0.1wt%) and the fine particle size rendered it visibly transparent but capable of greatly attenuating UV radiation in the full UV range. These novel hybrid inorganic-organic materials can be directly applied in the UV-shielding field. 1. Ahmad Z., Sarwar M. I. & Mark J. E. J. Mat. Chem. 1997, 7(2), 259 2. Schmidt H., Schloze H. & Tunker G. J. Non-Cryst. Solids 1986, 80, 557 3. Mitchnick M. A. et al. US patent 5, 733, 531

R8.46

A Study of the Structure of CeO/sub2 Nanoneedles and Nanorods. Natalia Bugayeva, School of Mechanical Engineering, University of Western Australia, Crawley, Western Australia, Australia.

It is commonly believed that morphologies and internal structure of nanoparticles greatly enhance mechanical, electrical and optical properties of materials. Ceria and doped ceria are very promising catalyst support and solid fuel cell materials. In the present work we investigate the structure of ceria nanorods and nanoneedles using high resolution transmission electron microscopy (HRTEM) and electron microdiffraction with dark field (DF) imaging techniques. The needle- and rod-like morphologies of hydrous ceria CeO/sub2 are obtained via a gel-sol technique. The needle-like particles are of length 800 - 1500 nm and diameter 10 - 60 nm, while the rod-like particles have lengths of 450 - 900 nm with diameters of 10 - 50 nm. HRTEM showed that needles have a fibrous structure consisting of a number of whiskers joined in bundles, whereas rods are single units with characteristic prismatic caps at the ends. HRTEM allowed the determination of the fringe spacings and angular relations of various lattice planes. Power spectra of HRTEM images of a single whisker of a needle and a rod show complex patterns that imply the particles are not single crystals or polycrystalline with randomly oriented subunits. The patterns indicate strongly ordered structures. From power spectra of HRTEM images the crystallographic orientations of subunits are identified, as [110], [111], [100] and [112]. All four patterns appear simultaneously in a complex one sharing one set of the reflection from {220} planes. This [220] crystallographic direction is a direction of the particle growth. Electron microdiffraction with DF imaging confirm these findings. DF image of a single whisker shows a finer structure demonstrating presence of subunits. Electron microdiffraction patterns from different subunits of a particle are obtained. The diffraction patterns are characteristic for [111], [110] and [112] crystallographic orientations. A model for a rod-like morphology is proposed to explain a possible mutual orientation of subunits. It consists of a number of tetrahedra arranged around a longitudinal

axis of a particle. The model exhibits five-fold symmetry and multiple twinning around {111} planes of fcc structure. Properties of the model explain all experimental data including the simultaneous presence of four patterns, deviations in planar angles and distances as well as the growth direction of the particles. According to the model ceria nanorods can be classified as quasicrystals. The complex internal structure and the shape anisotropy should influence the properties of the nanoparticles making ceria nanoneedles and nanorods very interesting for the further study and applications.

R8.47

Evaluation of POEA/PSS Layer-by-Layer Films for Electronic Tongue. Nadja Karolina Leonel Wiziack¹, Leonardo G. Paterno^{2,1}, Fabio H. Kanno¹, Fernando Josepatti Fonseca¹ and Luiz Henrique Capparelli Mattoso²; ¹Dep. de Engenharia de Sistemas Eletronicos, Universidade de Sao Paulo, Sao Paulo, SP, Brazil; ²Instrumentacao Agropecuaria, EMBRAPA, Sao Carlos, SP, Brazil.

Electronic tongues are sensory systems able to detect and discriminate substances in liquid phase. Usually those systems are composed of an array of non-specific sensors whose electrical response is interpreted by multivariate data analysis. Recently it has been demonstrated that layer-by-layer (LBL) films of conducting polymers can be used as sensing parts in these kind of sensory systems [1,2,3]. In our investigations we have verified that the electrical response of LBL films of poly(o-ethoxyaniline) POEA and sulfonated poly(styrene) PSS could be regulated by the number of POEA/PSS bilayers deposited. According to the AC impedance data the capacitance of the films deposited onto gold interdigitated microelectrodes and immersed into different liquids has increased when more bilayers were adsorbed. For instance, the capacitance measured for a 1 bilayer film immersed in NaCl 5mM at 100Hz was found 81 nF and increased to 234 nF for a 5 bilayer film and 594 nF for a 10 bilayer film. This behavior was repetitive and reproducible in different experiments for different liquids. It has been also observed that the electrical response of POEA/PSS films is reversible and independent on the number of bilayer adsorbed. Therefore, POEA/PSS LBL films with different sensitivities for liquids can be fabricated by varying the number of POEA/PSS bilayers deposited demonstrating the possibility of their utilization as sensing parts in an electronic tongue. [1] Riul Jr., A., Malmegrim, R.R.; Fonseca, F.J.; Mattoso, L.H.C. An artificial taste sensor based on conducting polymers - Biosensors - Bioelectronics, v.18, p.1365-1369, 2003. [2] Riul Jr., A.; Malmegrim, R.R.; Fonseca, F.J.; Mattoso, L.H.C. Nano-assembled films for taste sensor application - Artificial Organs, v.27, n.5, p.457-460, 2003. [3] Santos Jr, D. S., Riul Jr, A., Malmegrim, R. R., Fonseca, F.J., Oliveira Jr, O. N., Mattoso, L. H. C. A layer-by-layer film of chitosan in a taste sensor application. Macromolecular Bioscience, v.3, p.591 - 595, 2003.

R8.48

Synthesis and Electrochemical Characterization of Carbon Electrode-Immobilized Glucose Oxidase with Gold Nanoparticle Mediator. Ying-Ying Horng¹, Li-Chyong Chen²,

Kuei-Hsien Chen^{2,3} and Chia-Chun Chen^{1,3}; ¹Chemistry, National Taiwan Normal University, Taipei, Taiwan; ²Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; ³Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

We demonstrated the synthesis and related electrochemical properties of enzyme, glucose oxidase (GOx), modified carbon cloth electrodes which are mediated by gold nanoparticles (Au NPs) in this report. The Au NPs with an average diameter of 4 nm are used as a significant electron relay or mediator for the alignment of the GOx on the carbon support. At the same time, the GOx is immobilized by flavin adenin dinucleotide cofactor on Au NPs. Therefore, the biological catalysts, GOx, become much more stable on conductive carbon supports. Moreover, cyclic voltammetry are used to study the electrochemical behavior in a three-electrodes system. The results show that immobilized GOx is able to maintain its substrate specific enzyme activity in the presence of glucose. Furthermore, the dependence of current density and the redox potential in the corresponding reaction is also investigated. As a consequence, under optimal condition, good electrochemical behavior and large current can be achieved, thereby indicating the potential application in biofuel cells.

R8.49

Excellent Antireflection Properties of Controllable GaAs Nanotip Arrays. Fu-Kuo Chiang¹, Hung-Chun Lo², Yi-Fan Hwang³,

Chih-Hsien Hwang¹, Li-Chiung Chen¹ and Kuei-Hsien Chen²; ¹Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan; ²Department of Materials Science and Engineering, National Chiao Tung University, Hsin-chu, Taiwan; ³Institute of Mechanical and Electrical Engineering, National Taipei University of Technology, Taipei, Taiwan; ⁴Institute of Optoelectronic Sciences,

National Taiwan Ocean University, Keelung, Taiwan; ⁵Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan.

Gallium arsenide (GaAs) nanotip arrays have been produced by using the self-masked dry etching (SMDE) technique in the electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-CVD) reactor. The morphology evolution and nanoscale structure of the GaAs nanotip have been examined using high resolution scanning electron microscope (HR-SEM) and transmission electron microscope (TEM). The lengths of the nanotip arrays can be controlled from 0.1 μm to 3 μm by tuning the reaction parameters. Furthermore, the optical reflectance of various GaAs nanotip arrays has been carefully investigated by integral sphere measurement. It is found that the nanotip arrays exhibit ultra low reflectance, which is less than 0.5% in UV-VIS range (200 ~ 1000 nm), indicating an excellent antireflection (AR) property for wide range applications such as solar cells. The experimental results agree well with theoretical simulation based on the rigorous coupled-wave analysis (RCWA) and the theory of electromagnetic wave scattering from random rough surface, which were used to simulate the gradient index and the reflectance of the nanotip arrays, respectively.

R8.50

Synthesis and Characterization of Sol-Gel Derived MgO Monoliths. Winny Dong¹, Jeffrey S. Sakamoto², Jesse Rivera¹, Celia

Tang¹ and Elizabeth Yen²; ¹Chemical and Materials Engineering, California State Polytechnic University, Pomona, Pomona, California; ²Jet Propulsion Laboratory, Pasadena, California.

Sol-gel derived magnesium oxide aerogels and xerogels have many applications such as humidity sensors, hydrolysis catalysts, bactericidal agents, and as protective layers in plasma display panels. Like most transition metals, magnesium is highly hydroscopic and reacts rapidly with water in the sol-gel process. This has resulted in mostly thin films and powders of MgO aerogels and xerogels being reported. We have successfully synthesized stable MgO aerogel and xerogel monoliths with gelation times of up to 10 minutes. This is achieved with the use of glycerol and acetic acid as chelating ligands. The roles of the ligands are investigated in the MgO gelation process via FTIR, XRD, and TGA/DSC. The physical properties, including surface area, density, and high temperature stability of the MgO monoliths are also examined.

R8.51

Characteristics and Applications of Nanostructured Nitrides Synthesized by Vapor Phase Reactions. Gerald Ziegenbalg, Carsten Paetzold, Ute Singliar and Rico Berthold; Institute of Technical Chemistry, TU Bergakademie Freiberg, Freiberg, Germany.

Vapor phase synthesis is a well known way to produce oxides such as SiO₂ and TiO₂. Only little is known about synthesis paths leading to nitrides and the characteristics of the resulting powders. Compounds such as tungsten, molybdenum or titanium nitride, however, offer many new applications in catalysis or gas separation. The same is true for silicon or boron nitride or mixtures of different nitrides. The paper summarizes comprehensive investigations to prepare nonoxidic nanoparticles by vapor phase synthesis and gives an overview about the reaction mechanism leading to powder formation. First applications of nitrides for gas adsorption or as catalysts are discussed. The ammonolysis of volatile halogenides is a multistep process characterized by an overlapping of gas-gas and gas-solid reactions. Ammonium chloride is formed as byproduct after cooling of the synthesis gases and has to be removed in a separate processing step. Uniform, spherical nanoparticles are obtained with particle sizes between 20 and 300 nm. The specific surface can reach up to 300 m²/g. Both crystalline and amorphous compounds are formed. Ammonolysis of SiCl₄ or BCl₃ results in amorphous, chloride containing intermediates. After treatment in ammonia is necessary to obtain chlorine free products. Crystalline phases of tungsten, molybdenum or titanium nitride are formed at temperatures above 800 °C. Ammonolysis of mixtures of halogenides gives mixtures of the corresponding nitrides or leads to ternary or higher nitrides. Their composition depends on the reactivity of the used halogenides as well as the reaction conditions such as temperature, input gas composition and retention time. For example, ammonolysis of SiCl₄/TiCl₄ mixtures at 1000 °C results in crystalline TiN nuclei that are overlaid by amorphous Si-N-(H)-Ti-Cl compounds. First investigations have shown that silicon nitride or silicon oxynitrides are favorable basic supports. After deposition of platinum on the materials the obtained catalysts are catalytically active and selective for propane dehydrogenation. In comparison to well known Pt/MgO materials Pt/SiN catalysts are characterized by higher catalytic activity, propene selectivity and stability. A remarkable improvement of the catalytic properties was found after incorporation of small amounts of boron, carbon and titanium in the support material. Amorphous silicon nitride is able to adsorb reversibly up to 7 wt.-% NH₃, 10 wt.-% SO₂ or 4 wt.-% CO₂ at 25 °C. The adsorption

depends on the composition of the used material, temperature and the input gas composition. Apart from ammonia decomposition tungsten or molybdenum nitrides are catalytically active in many reactions such as hydrogenation, dehydrogenation, isomerization or amination. Selected reactions will be discussed, especially in respect to the long time stability of the nitrides.

R8.52

A Widely Applicable Synthetic Approach of Multimetallic Oxides from Hybrid Organic-inorganic Materials Made of Ordered Functionalized Polymeric Matrices and Inorganic Salts. F. Rullens¹, A. Laschewsky² and M. Devillers¹; ¹Chemistry, Catholic University of Louvain, Louvain-la-Neuve, Belgium; ²Fraunhofer Institut fuer Polymerforschung, Golm, Germany.

A promising and widely applicable pathway to prepare multimetallic oxides was developed and applied to the preparation of M^1-M^2-O systems as bulk phases, supported phases, or thin films. This approach was based on homogeneous hybrid inorganic-organic structures in which specially-designed and functionalized ampholytic copolymers were used as matrices to stabilize inorganic species in aqueous solutions. These systems were then used as novel precursors for the manufacture of inorganic materials under soft conditions. The poly(ampholyte)s selected in this work result from the association of monomers bearing carboxylic acid (maleic or maleamic acids) or amine (modified diallylamine/diallylammonium) moieties. They constitute particularly interesting matrices because of their tunable properties: number of functional groups of each type (point of zero charge, pH-window for stability,...), presence of additional substituents, such as alkyl chains of different lengths (C_6 , C_{12} and C_{18}) able to induce a supramolecular organization, presence of charged or complexation sites efficient for interacting with cations, and solubility in various polar media. This new route was applied to two model systems: (i) simple or mixed 3d transition metal molybdates ($M^1_x M^2_{1-x} MoO_4$, with M^1 , $M^2 = Ni, Co, Mn$), in their unsupported or silica-supported forms, and (ii) bismuth vanadates ($BiVO_4$, $Bi_4V_2O_{11}$) as bulk phases or thin films on glass/quartz substrates. The metal precursors used were the metal (Ni, Co, Mn, Bi) nitrates, ammonium (hepta)molybdate, or ammonium metavanadate. Hybrid materials were prepared from some of the copolymers synthesized and inorganic salts. The interactions between the polymer and the inorganic species were studied, in solution (UV-vis-NIR, NMR) as well as in the solid state (XRD, Raman, UV-vis-DRS). Under controlled pH conditions, homogeneous solutions are obtained, in which the interactions between the cations and the polyampholyte appear to be essentially electrostatic, even if complexation can be assumed to take place under certain conditions. Powdered hybrid materials were finally obtained by simple removal of the solvent under reduced pressure or lyophilisation. In the molybdate system, ordered or amorphous materials were obtained, depending of the copolymer, and the homogeneity was kept up to 2 equivalents of metal ion (cationic as well as anionic) introduced for 1 repeat unit of the polymer. Characterization of the final molybdate phases by XRD and Raman spectroscopy indicated that the α - as well as the β -phases could be prepared, and that the mixed structures were solid solutions of the simple $NiMoO_4$, $MnMoO_4$ and $CoMoO_4$. In the case of bulk Bi vanadates, $BiVO_4$ and γ - $Bi_4V_2O_{11}$ could be obtained as pure phases for the molar ratios Bi/V of 1 and 2, respectively. Thin films of the $BiVO_4$ phase were also prepared by spin-coating and subsequent drying and calcination of the hybrid layer.

R8.53

Growth and Luminescence from Ga2O3 Nanowires and Nanoneedles. Emilio Nogales, Bianchi Mendez and Javier Piquerias; Fisica de Materiales, Universidad Complutense de Madrid, Madrid, Spain.

Ga₂O₃ nano- and microwires with transversal dimensions ranging from tens of nanometers to about one micron and lengths of up to tens of microns, have been obtained on the surface of disks of compressed Ga₂O₃ powder during sintering at 1500 °C under argon flow. The elongated structures were obtained only during the treatments performed at a narrow temperature range, around the mentioned value, while the parameters of the argon flow are also critical to favour the growth of the wires. By increasing annealing time, the formation of sheets terminating in micro and nanoneedles, which has been sometimes described as comb-like structure, is observed. Similar structures were reported for CdSe sintered under argon flow (1). The elongated structures have been investigated by cathodoluminescence (CL) in the scanning electron microscope. The starting powder shows a blue-green CL emission with peaks at about 2.5 eV and 2.9 eV which have been previously reported for Ga₂O₃. After the thermal treatment, the green component is absent while a broad band centered at 3.3 eV and a red emission at about 1.73 eV, which is intense even at room temperature, are observed. Comparison of samples treated in argon and in nitrogen shows that the red band does not appear to be directly related to nitrogen. Spatially resolved

CL spectra show that the relative intensity of the red band is higher in the nanowires and in the comb like structures than in the sample background. The emission is composed of a broad band and a series of sharp peaks separated 20 meV which are the main features at low temperatures. The relationship of the red emission with intrinsic defects or impurities in the nanowires, in particular the presence of DAP transitions, is discussed. 1) A.Urbieta, P.Fernandez and J.Piquerias, Accepted in Appl. Phys.Lett.

R8.54

Optimized Silver Film over Nanosphere Surfaces for the Biowarfare Agent Detection Based on Surface-Enhanced Raman Spectroscopy. Xiaoyu Zhang and Richard P. Van Duyne; Chemistry, Northwestern University, Evanston, Illinois.

This work presents the rapid detection of *Bacillus subtilis* spores, harmless simulants for *Bacillus anthracis*, using surface-enhanced Raman spectroscopy (SERS) on silver film over nanosphere (AgFON) substrates. Calcium dipicolinate (CaDPA), a biomarker for bacillus spores, can be effectively extracted from spores with nitric acid and successfully detected by SERS. The highly tunable nature of AgFON's optical properties was exploited to optimize detection conditions. AgFON surfaces optimized for the near IR laser excitation were characterized and evaluated by UV-vis diffuse reflectance spectroscopy and SERS. The data presented herein also demonstrated that the storage life of AgFON substrates is at least 40 days. The SERS signal from extracted CaDPA was evaluated over the spore concentration range 10^{-15} - 10^{-12} M to determine the adsorption capacity of the AgFON substrate and the limit of detection. These sensing capabilities have been successfully transitioned to an inexpensive, compact Raman spectrometer. Using the extraction method and this field-portable instrument, the anthrax infectious dose of 10^4 spores were detected with only a five-second collection period on a one-month old prefabricated AgFON substrate.

R8.55

Behavior of Freezing and Melting of Methane in Microporous Material with Heterogeneous Surfaces of Rectilinear Groove. Yang Gon Seo¹, Mark Biggs², Alex Butts² and Nigel Seaton²;

¹Department of Chemical and Biological Engineering, Gyeong Sang National University, Jinju, South Korea; ²Institute for Materials and Processes, University of Edinburgh, Edinburgh, United Kingdom.

An understanding on melting and/or freezing phenomena in porous materials is important for many applications in areas relating to the fabrication of nanomaterials, the nanoporous solid characterization, and the behavior of fluids in the surface force apparatus. This can also lead to significant improvement on understanding fluid behavior in adsorption processes, membrane separations, and catalytic reactions in the chemical and oil industry, where meso and microporous material as adsorbents or supports are widely used. Many experimental and theoretical studies of melting and freezing in porous material have been reported during the past two decades. In many of studies porous Vycor glasses and activated carbons were used, and these studies usually show that the melting temperature is depressed or elevated on confinement as compared with bulk melting temperature, and that hysteresis is associated with the transition. For theoretical and simulation works the molecular structure of the adsorbate is known. However, with exception of the crystalline materials, one of the greatest difficulties is in determining the morphology of the materials. The majority of previous theoretical studies on elevated freezing in nanoporous system is based on simple geometries such as slit and cylindrical pores. Simple models restrict interpreting results for more realistic pore structures; therefore, extension to more complex models included elements of reality is necessary. Few of the studies in more complex pore spaces considered freezing transition and associated solidlike phases. A grand canonical Monte Carlo simulation has been used to simulate freezing and melting phenomenon of a Lennard-Jones fluid modeled on methane in a carbonaceous material with heterogeneous surfaces of rectilinear groove. Two types of pore models were considered; one is removing portion of carbon atoms on the only first layer from slit-shaped pore and the other is removing up to second layer. As well as changes in the overall properties of the adsorbate phase, corresponding changes in the individual adsorbate layers in the model pore were studied from a sufficiently high temperature to low temperature much lower than bulk freezing point of the model fluid. At sufficiently low temperature hexagonal and locally orthorhombic configuration coexisted in same layer due to the ability to physically accommodate adsorbate and defects of solid surfaces. For both pores freezing occurred nonuniformly through the pore space and even in each adsorbed layers, and the fluid structure at sufficiently low temperature was not ideal due to defects of solid surface. For each system only first layer which contacts with solid wall in ditch was shown an abrupt increase in two-dimensional density. This abrupt increase was caused by the formation of new seed to grow solidlike phase and move of adjacent two seeds. This phenomenon related local melting/refreezing processes.

R8.56

Optical and Electrical Switching Properties of Gadolinium - Gadolinium Hydride / Palladium Silver System.

Heinz Schmitt¹ and El Sayed Shalaa²; ¹Technical Physics, Saarland University, Saarbruecken, Saarland, Germany; ²Technical Physics, Saarland University, Saarbruecken, Saarland, Germany.

A remarkable discovery by Huilberts et al. has initiated a large interest in metal hydrides [1]. Thin Palladium capped rare earth metallic films switch reversibly from their initial reflecting state (metal phase) to visually transparent state (insulator or semiconductor phase) when exposed to gaseous hydrogen. E.g. metallic Yttrium films transform via an intermediate Yttriumdihydride phase (YH₂) to Yttriumtrihydride (YH₃). Reversion to the reflecting state can be achieved by exposure to air. This optical switch can be used as well in display and information technology as in switchable smart windows. The Palladium cap prevents oxidation and catalyzes hydrogen absorption and desorption at room temperature. The disadvantages of YH₃ films with a Palladium (Pd) top layer are the color of the YH₃-films and the reduced transparency caused by the Pd-film. The use of Gadoliniumhydride films (GdH₃) instead of YH₃ shifts the absorption edge to lower wavelengths. This effect can be improved by the modification of the films by Magnesium (Mg). Gd- and (GdMg)-films as well as top layers of catalytic films were prepared by rf-sputtering technique. To improve the optical properties, optical transparency, color and switching time, the Gd films were modified with Mg. By change of the sputtering parameters, additionally the grain size of the Gd-films was varied in the range from 29 nm to 9.5 nm. To improve the catalytic properties, the Pd-films were modified with Silver. X-ray diffraction measurements show, that the metallic Gd films are hexagonal, and - dependent on the sputtering conditions - with a strong preferential orientation in 002-direction. Because there are a few reflexes only, the grain size was calculated by the Scherrer equation using the 002-reflex. If the Gd-Pd-films are exposed to Hydrogen (at normal pressure) the Gd-film makes a transformation to GdH₃ which is found to be cubic. Investigations with a Scanning electron microscope show, that on float glass as substrates, the films are dense and free of cracks if they are in the thickness range below of about 300 nm. It is shown that the optical transmission of the GdH₃ films can be improved by the incorporation of Mg into the Gd-films. There is also a significant influence of the grain size of the films. If the grains size of the films is reduced to 9.5 nm, the optical transmission of the films increases. The reduced grain size, leading to a larger inner surface, decreases as well the optical as the electrical switching time. An additional significant reduction of the switching time is attained by the incorporation of Silver into the Palladium films. [1] J. N. Huilberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot, and N. J. Koeman, Nature (London), 380, 231, (1996).

R8.57

Nanowire Avalanche Photodiodes. Oliver Hayden^{1,2} and Ritesh Agarwal¹; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Institute of Analytical Chemistry, University of Vienna, Vienna, Austria.

Electrically-driven nanowire devices showing gain, such as nanowire FETs, are of importance for their applicability as sensors. The same is true for photonic applications where gain is needed to detect very low light intensities on the nanoscale. Here, we report the fabrication and characterization of single nanowire avalanche photodiodes (nanoAPDs) as well as nanoAPD arrays. NanoAPDs were formed by the assembly of p-doped silicon nanowires and n-type cadmium sulphide (CdS) nanowires in crossed wire architecture. The devices were fabricated by fluid-directed assembly of the nanowires on oxidized silicon substrates. Temperature dependent measurements of the current-voltage characteristic were performed to reveal the breakdown mechanism. We observed Zener at high p-Si doping and avalanche breakdown mechanism at low p-Si doping. The photocurrent intensity was spatially resolved by laser scanning of the nanowire crossing. The highest photocurrent was measured with the laser positioned at the crossing of the nanowires with a detection limit of ~ 50 photons. The implications of these results for highly integrated photonic devices and optoelectronics will be discussed. This work was performed in the laboratory of Prof. Charles M. Lieber.

R8.58

Morphology, Structure and Optical Properties of MOCVD Grown Nanowires of ZnxCd1-xSe Pseudo-Binary Alloys on Si and GaAs Substrate. Ching-man Ng, C. X. Shan and S. K. Hark; Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

Long and fine nanowires of Zn_{1-x}Cd_xSe pseudo-binary alloys of various compositions x covering the entire range were grown by metalorganic chemical vapor deposition, using diethylzinc,

dimethylcadmium and diisopropylselenide as precursors, on Si (100), GaAs (100) and GaAs (111) substrates, sputtered coated with a thin layer of gold as a catalyst. By controlling the ratios of the flows of the precursor, the temperature and pressure during growth, we obtained nanowires of desired composition. The morphology, structure and optical properties of the structures were studied by various techniques, including secondary electron microscope, atomic force microscope, transmission electron microscope, x-ray diffraction, photoluminescence, and Raman scattering. Depending on the substrate, composition and conditions of growth, either the zincblende or wurtzite forms could be obtained. Epitaxy on GaAs, give rise to well-aligned zincblende nanowires, even at compositions where the stable form should have been wurtzite. On GaAs (100), the nanowires grow along four physically equivalent directions; on GaAs (111) they tend to grow along three. From the orientations of these nanowires on the surface, their directions of growth was deduced and confirmed by high resolution lattice imaging. The relationship between the band gap and composition of the nanowires were measured and found to deviate from that of bulk alloys or epilayers. The interplay between conditions of growth and composition and morphology of the nanowires will be discussed.

R8.59

Binding of Water Molecules to Protozeolitic Nanoclusters.

Subhendra D. Mahanti¹, Hong Li¹ and Thomas J Pinnavaia²;

¹Physics and Astronomy, Michigan State University, East Lansing, Michigan; ²Department of Chemistry, Michigan State University, East Lansing, Michigan.

Protozeolitic nanoclusters, also known as "zeolitic seeds" are disordered aluminosilicate polyanions that nucleate the crystallization of specific zeolite structure types. They are essential precursors in zeolite synthesis and can only be formed through coordinative interactions with specific structure-directing counter-ions. When incorporated into the framework of amorphous mesostructured aluminosilicates (a-MAS), zeolite seeds greatly enhance the hydrolytic stability of the framework in comparison to analogous derivatives assembled from conventional aluminate and silicate precursors.[1] NMR and IR spectroscopy in a-MAS give unequivocal evidence for local structure analogous to the secondary building units of zeolites. The key to understanding the differences in hydrolytic stability among these formally amorphous framework structures rests on our ability to elucidate local nanostructures and their interaction with water molecules. Ab initio density functional calculations have been carried out to investigate the structure and bonding of silica and aluminosilicate (AS) clusters containing 5- and 6-membered oxygen rings, modelling protozeolitic nanoclusters. Two locally different Bronsted acid sites in the AS structure have been identified for the water binding sites. The question of hydrolytic stability has been studied by probing the energetics of breaking an Al-O bond and inserting a water molecule into the 5-membered ring structure. We find that an excitation energy of ~0.325 eV (nearly 13 times the thermal energy corresponding to room temperature 300K) is needed to break the stable 5-membered ring structure. This indicates the high hydrolytic stability of AS mesostructures into which zeolitic seeds (protozeolitic nanoclusters) have been inserted. Work partially supported by NSF-CRG grant CHE-0211029 [1] Y. Liu, W. Zhang and T. J. Pinnavaia, JACS, 122, 8791 (2000); T. Zhang et al., JACS 123, 5014 (2001); D. T. On and S. Kaliaguine, Chem. Int. Ed. Engl., 41, 1036 (2002).

R8.60

Mechanistic Studies of the Formation of Alumina Sol-Gels by Multinuclear NMR. Sarah C. Chinn, April M. Sawvel, Theodore F. Baumann, Joe. H. Satcher and Robert S. Maxwell; Lawrence Livermore National Laboratory, Livermore, California.

Sol-gel materials possess unique structural properties which have led to their use in a wide variety of applications including catalysts, ceramics, sensors/detectors, and nano-electronics. We recently reported the synthesis of high surface area alumina aerogels through the sol-gel polymerization of hydrated aluminum salts, AlCl₃·6H₂O or Al(NO₃)₃·9H₂O, using propylene oxide as the gelation initiator. This technique affords high surface area alumina aerogels without the use of highly reactive alkoxide precursors. In the course of that work, it was noted that the solvent and the anion of the Al(III) salt used in the sol-gel reaction had a significant impact on the structural and mechanical properties of the condensed alumina phase. In the work presented here, we are using multinuclear NMR spectroscopy to investigate the reaction mechanisms associated with the formation of these alumina materials. A combination of ¹H, ²⁷Al and ¹⁷O solution state and solid-state magic angle spinning experiments including multidimensional techniques such as MQMAS are being used to follow the kinetics of nucleation and growth of solution aggregates as well as their subsequent organization into the final sol-gel architecture. The results of these experiments will provide mechanistic information that can be used to reliably predict and control the bulk properties of

these sol-gel materials. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract # W-7405-ENG-48.

R8.61

Study on Structure and Growth of Nano-Sized Silica Clusters. Xin Liu, Changgong Meng and Changhou Liu; Department of Chemistry, Dalian University of Technology, Dalian, China.

Sol-gel procedures are widely used in synthesis of high quality microporous and mesoporous materials. In-depth understanding of the basic processes involved would help us to figure out how it happens and by which way we can get the desired material. The fundamental mechanisms are known to involve condensation and polymerisation of precursor nano-sized clusters, but there is still little insight information available. In this work, we firstly used ab initio methods to study structural and energies of small nano-sized silica clusters, containing from 1 to 5 Si atoms. All the structures were optimised with Hartee-Fork and DFT methods at 6-311G* level first, and confirmed to be the minimum point by the frequency analysis. All the calculation was done with Gaussian 98W (A. 7) software. And the structural data showed that condensation was mainly induced by the inter-molecular and intra-molecular hydrogen-bond. Several transition state of intra-molecular condensation reaction were located, and were found to be strongly affected by the conformation of the cluster. This phenomenon is more obvious for those clusters with a branched structure. Then full potential energy scan was carried out at RHF/6-311G* and B3LYP/6-311G* level to study the contribution of conformation on the condensation reaction. In order to locate the real minimum, scan on relaxed potential energy surfaces were also carried out. There are several local minimum on the conformational potential surface of these silica clusters. And the energy data showed that conformational potential energy surfaces are relatively smooth and the energy difference at different local minimum is very small. In this case, small changes in its surrounding condition will result in its conformational change, moving from one local minimum to another, especially in existence of organic template molecule. Finally, in order to study the condensation and polymerization reaction in detail at microscopic level, we performed large cluster calculation with the ONIOM method implemented with G98w software. Silica clusters and/or organic template molecules are embedded into large clusters of water molecules. We start from a large cluster containing only silica clusters first, to get their structure in water. And then the cluster was enlarge to include organic molecules. The resulting structural difference shows that existence of organic template molecule near the cluster will result in strongly altered conformation and structure of the silica cluster. The inter-molecular long-range forces due to interaction between the template ion and the silica cluster was found to be the driving force. Different template molecule produces difference final structure and further condensation reaction was observed taking place at a local minimum on the potential energy surface. This accounts for why so many different kind of silicon containing microporous and mesoporous can be synthesised with sol-gel method.

R8.62

Silica Nanofibers containing Transition Metal Oxides from Sol-gel/Electrospinning Processes. Jeanne E. Panels and Yong L. Joo; Chemical Engineering, Cornell University, Ithaca, New York.

Electrospinning is a fiber formation process which relies on electrical field rather than mechanical force to form fibers with diameters ranging from 100nm – 10 μ m. There has been growing interest in one-dimensional, inorganic nanosized materials including silica nanofiber mats for their high thermal stability and large surface to volume ratio. Recently a sol-gel precursor composed of TEOS, ethanol, water, and HCl has been electrospun during the sol-gel transition to produce silica nanofibers without using any binder. These silica nanofiber mats provide an ideal platform for the incorporation of transition metals for various applications including catalysis and sensing. In the present study, vanadium oxytriisopropoxide and iron nitrate are incorporated into silica nanofibers during sol-gel/electrospinning processes for gas sensing and for separation applications, respectively. Silica nanofibers containing these transition metal oxides are obtained by calcinating at 600 to 900 °C. These metal oxides have been incorporated into sol-gel synthesis to form thin films, but they have never been functionalized into inorganic fibers. The resulting functionalized silica nanofibers will take advantage of their high thermal stability and large surface areas. SEM studies show that functionalized silica fibers have diameters below 1 micron and that the size and its distribution of fiber dimension were preserved after calcination. The presence of transition metal oxides are confirmed by XRD and XPS experiments. The distribution of transition metal oxides in the silica fibers is investigated by TEM studies. The location of the metal oxide particles within the fiber is very important and we would eventually like to control the distribution of particles to the surface of the fibers

so that their sensing or superparamagnetic abilities can be used most effectively. Finally, the electrical resistance under a high input impedance and field dependence of magnetic properties of functionalized silica fibers will be presented.

R8.63

Vacancy Supersaturation and Nanocrystalline Microstructural Evolution. Moneesh Upmanyu¹ and Branden B. Kappes²; ¹Engineering Division, Materials Science Program, Colorado School of Mines, Golden, Colorado; ²Materials Science Program, Colorado School of Mines, Golden, Colorado.

Vacancy supersaturation is believed to retard motion of grain boundaries at the nanoscale. In this talk, we present molecular simulations aimed at quantifying this effect in pure Al. Non-equilibrium concentrations of (almost) immobile vacancies in the vicinity of a shrinking cylindrical grain facilitate grain boundary motion. These results unambiguously show that the vacancies sink action at the moving grain boundaries aids grain boundary motion. We expect these results to be relevant for nanocrystalline microstructural evolution in systems with no other sinks for vacancies. Details of the modified kinetic mechanisms, as well as the effect of voids and pores will also be presented.

R8.64

Novel Chemical Sensor Concept for Neutral Radical Detection in Gas Phase. Vladislav Vladimirovich Styrov¹,

Alexander Y. Kabansky², Victor P. Grankin³, Stanislav Kh. Shigalugov⁴ and Yury I. Tyurin⁵; ¹Physics Department, Azov State Technical University, Mariupol, Ukraine; ²R&D Department, Cypress Semiconductor, San Jose, California; ³Computer Simulation and Modeling, Azov State Technical University, Mariupol, Ukraine; ⁴Physics Department, Noril'sk Industrial Institute, Noril'sk, Russian Federation; ⁵Physics Department, Tomsk Polytechnic University, Tomsk, Russian Federation.

The problem of detection of atomic and molecular radicals is of great importance for space technologies, for monitoring the atmospheres of Earth and other planets, for diagnostics of plasma-chemical processes, for ecological needs, etc. The most urgent radicals are H, O, N, OH, NO, CO, CH_x, etc. Conventional solid chemical sensors for detecting gaseous species utilize an effect of variation of their electrical characteristics due to adsorption mechanism, but have poor selectivity and response time. In this paper we present a concept of novel real-time chemical sensors which sensing mechanism can be described as direct electron excitation of semiconductor material due to chemical energy released in heterogeneous reactions of gaseous species on its surfaces [1]. The related non-equilibrium electronic phenomena comprise: (i) light emission from solid surfaces (heterogeneous chemiluminescence-HCL) caused by chemiexcitation of surface states, (ii) chemivoltaic effects, initiated by electron-hole (e-h) pair injection into semiconductor due to surface chemical reactions, (iii) chemielectron emission from surfaces with low work function. It was proved that chemieffects listed above are analogous to corresponding photoeffects (photoluminescence, photo-voltaic effects, etc.). The major difference is that the chemieffects are originated from the surface during chemical reactions of gaseous radicals and very selective to radical type, sensor material and surface preparation. They also provide a new means for in-situ gas/solid surface reaction studies [2]. More details of sensing mechanism, sensor performance and gas/solid reaction dynamics will be discussed. 1. Conventional phosphors are good candidates for chemiluminescent chemical sensors. The HCL spectra and kinetics are different for various gaseous reactive species and can be used for ensuring sensor selectivity and sensitivity. For the most promising phosphors, ZnS-Tm, ZnS-Cu, the cross-section of surface recombination of H-radicals is as large as ~10-17 cm²; a number of photons emitted from the surface per radical recombination event (quantum yield of HCL) being 10-2-10-4. These parameters lead to HCL sensor sensitivity for H-radicals up to 10⁶ at/cm³. Surface-activated phosphors, nano-phosphors (with large surface-to-volume ratio), other promising materials and catalysts will be highlighted as well as experimental results and computer modeling data. 2. The small band gap semiconductors, such as Ge, CdS and ZnSe, demonstrate high efficiency of e-h pair generation during H-atom heterogeneous recombination. For example, in Ge this efficiency reaches 0.6 pairs per chemical reaction event. The corresponding effects in p-n junction (chemi-EMF) or in transversal magnetic field (chemi-magnetic EMF) can be employed as an effective means for radical detection. Sensor characteristics and integration into planar MOS technology will be discussed. [1] V. P. Grankin, V.V. Styrov, *Physica Scripta* T108, 33 (2004)

8:00 AM *R9.1/P6.1

The Role of Atomic Resolution-In Situ Electron Microscopy in the Development of Nanomaterials for Green Chemical Catalysis and New Energy Carriers. Pratibha L. Gal, ¹Central Research and Development, DuPont, Wilmington, Delaware; ²Materials Science, University of Delaware, Newark, Delaware.

Global challenges of the 21st century include sustainable alternative energy sources, energy carriers and novel green routes to polymers. Today, our world faces a variety of challenges in creating alternative energy sources, reducing green house gases and toxic byproducts. The development of advanced methods in the design of molecular and nanomaterial systems are needed to meet these challenges. In situ atomic resolution-environmental electron microscopy (ETEM) is a powerful method in understanding and predicting how dynamic catalysts work at the atomic scale. In this presentation, I will describe the first in situ atomic resolution environmental-TEM (ETEM) developed in our laboratory to study dynamic gas adsorption on the surface of nanocatalysts and carbon nanostructures to engineer nanomaterials to meet these demands. The ETEM is capable of atomic resolution under gas pressures of a few mbar and temperatures up to 1000 C and gas-solid reactions can be monitored as they take place. Probing reactions in wet environments is also possible. Most recently, our research is focused on the heterogeneous hydrogenation routes using nanocatalyst materials in clean polymer technology. In addition, we have investigated nanomaterial architectures based on doped-carbon nanotubes and related nanostructures as candidates for hydrogen gas adsorption. The results exemplify the pivotal role of advanced in situ electron microscopy methods in the design of optimum nanomaterials for catalysis and energy storage.

8:30 AM *R9.2/P6.2

Understanding Growth Mechanisms and Kinetics of Gas Solid Interactions at Nanoscale using Environmental Transmission Electron Microscope. Renu Sharma, Center for Solid State Science, Arizona State University, Tempe, Arizona.

Transmission electron microscopy (TEM) has been the technique of choice for chemical and structural characterization of nanomaterials due to their infinitesimal size. Recent advances in the instrumentation have made it possible to obtain near atomic level information of the nanoscale synthesis processes in controlled gas pressures (up to 50 Torr) and high temperature (1000 C). These microscopes are commonly known as environmental transmission electron microscope (ETEM) and may be equipped with a field-emission gun (FEG). An ETEM is often used to understand the response of nanoparticles to gaseous environment and temperature at an atomic level and provides a powerful combination of in-situ imaging, diffraction and spectroscopy to obtain gas-solid reaction mechanisms of individual particles. Whereas high-resolution images and electron diffraction provide structural information, electron energy-loss spectroscopy (EELS) is used to obtain chemical information. Time and temperature resolved images and/or spectroscopic data provide the reaction rates that are used to obtain kinetic and thermodynamic data. Moreover, ETEM can also be used as a nanoscale cold-wall chemical vapor deposition (CVD) reactor, and is used to obtain nucleation and growth mechanism of nanomaterials during CVD process under diverse precursor pressure and deposition temperature. This unique combination of synthesis and characterization has tremendous time advantage over ex-situ synthesis and characterization. Practical applications of such microscope can be divided in to two broad categories: (1) transformation mechanism of nanostructures due to gaseous environment at elevated temperature and (2) controlled synthesis of nanomaterials. The first category includes examples of oxidation-reduction of catalysts e.g. three-way catalysts commonly used in catalytic converters of automobiles. The second category includes synthesis of carbon nanotubes, electron beam induced deposition of nanoparticles. Some examples form each category will be presented to elucidate different types of information that can be extracted from the in-situ data obtained using a FEG-ETEM.

9:00 AM R9.3/P6.3

Understanding Catalysis Through Aberration-Corrected STEM and Theory. Albina Y Borisevich¹, Andrew R. Lupini¹, Sanwu Wang², Sergey N. Rashkeev^{1,2}, Sokrates T. Pantelides^{2,1}, Karl Sohlberg³ and Stephen J. Pennycook^{1,2}; ¹Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee; ³Department of Chemistry, Drexel University, Philadelphia, Pennsylvania.

Aberration-corrected Z-contrast (HAADF) STEM offers unprecedented insights into the structure and functionality of heterogeneous catalysts due to its sub-Angstrom resolution and high sensitivity. Realistic catalysts such as high-surface area powders can be studied, and structural detail down to a single heavy atom (inside a lighter material or on its surface) can be detected. Such observations also provide a direct link to first-principles calculations, which can connect the structure of metal formations on oxide supports with the properties of the catalytic system. In the studies of La-doped γ -Al₂O₃ catalytic supports, the single-atom imaging and theoretical calculations allowed identification of isolated La atoms adsorbed on γ -Al₂O₃ surface as the instruments of the dopant-induced thermal stabilization [1]. In a related system, accurate measurements of the interatomic distances of the Pt₃ clusters on the surface of γ -Al₂O₃ and thorough theoretical analysis led us to discover that these units are capped with OH-groups, which affect electron density distribution within the clusters and, consequently, the catalytic activity of the system [2]. Simultaneously acquired electron energy loss (EELS) spectra were instrumental in characterizing distinct additive distribution for Cr₂O₃ on γ - and η -Al₂O₃. Additional possibilities open for the studies of bimetallic catalysts, where distribution of the two different metals can be addressed both by imaging (e.g. (Pt, Ru)/ γ -Al₂O₃) and by EELS (e.g. (Pt, Fe)/ γ -Al₂O₃ and MgO). Results on the study of three-dimensional structure of catalysts using a novel technique of depth slicing in STEM will also be discussed. [1] S. Wang, A. Y. Borisevich *et al.*, *Nature Materials* **3**, 143 (2004). [2] K. Sohlberg *et al.*, *Chem Phys Chem*, in press (2004).

9:15 AM R9.4/P6.4

The Effect of Substrates/Ligands on Metal Nanocatalysts Investigated by Quantitative Z-Contrast Imaging and High Resolution Electron Microscopy. Huiping Xu¹, Noel T. Nuhfer², Laurent Menard³, Anatoly Frenkel⁴, Ralph Nuzzo³, Duane Johnson³ and Judith C. Yang¹; ¹Dept of Mat Sci & Engr, University of Pittsburgh, Pittsburgh, Pennsylvania; ²Carnegie-Mellon University, Pittsburgh, Pennsylvania; ³University of Illinois at Urbana-Champaign, Urbana, Illinois; ⁴Yeshiva University, New York, New York.

Our direct density function-based simulations of Ru-, Pt- and mixed Ru-Pt clusters on carbon-based supports reveal that substrates can mediate the PtRu₅ particles [1]. Oblate structure of PtRu₅ on C has been found [2]. Nevertheless, the cluster-substrate interface interactions are still unknown. In this work, we present the applications of combinations of quantitative z-contrast imaging and high resolution electron microscopy in investigating the effect of different substrates and ligand shells on metal particles. Specifically, we developed a relatively new and powerful method to determine numbers of atoms in a nanoparticle as well as three-dimensional structures of particles including size and shape of particles on the substrates by very high angle (~96mrad) annular dark-field (HAADF) imaging [2-4] techniques. Recently, we successfully synthesized icosahedra Au₁₃ clusters with mixed ligands and cuboctahedral Au₁₃ cores with thiol ligands, which have been shown by TEM to be of sub-nanometer size (0.84nm) and highly monodisperse narrow distribution. X-ray absorption and UV-visible spectra indicates many differences between icosahedra and cuboctahedral Au₁₃ cores. Particles with different ligands show different emissions and higher quantum efficiency has been found in Au₁₁ (PPH3) SC12)2Cl₂. We plan to deposit those ligands-protected gold clusters onto different substrates, such as, TiO₂ and graphite, etc. Aforementioned analysis procedure will be performed for those particles on the substrates and results will be correlated with that of our simulations and activity properties. This approaching will lead to well understanding the cluster-substrate relationship for consideration in real applications. [1]. S. V. Khare, D.D. Johnson, A. Rockett, T. Martinez, A. I. Frenkel, R. G. Nuzzo, submitted (2004). [2]. J.C. Yang, S. Bradley, J.M. Gibson, *Materials Characterization*, **51**, 101 (2003). [3] J.C. Yang, S. Bradley and J.M. Gibson, *Microsc. Microanal.*, **6**, 353 (2000). [4]. A. Singhal, J.C. Yang and J.M. Gibson, *Ultramicroscopy*, **67**, 191 (1997). Supported by the Department of Energy (#DE-FG02-03ER15475).

9:30 AM R9.5/P6.5

Surface Defects on TiO₂(110): From Atomic and Electronic Structure to Catalytic Activity. Ken Taesung Park^{1,2}, Minghu Pan², Sergei Kalinin³, Vincent Meunier⁴, William Shelton⁴, Arthur P. Baddorf³ and E. Ward Plummer^{2,3}; ¹Physics, Baylor University, Waco, Texas; ²Physics and Astronomy, University of Tennessee, Knoxville, Tennessee; ³Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ⁴Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The chemical reactivity of solid surfaces is determined by the presence of active sites such as defects, vacancies, and step edges. Optimization of the catalytic and sensing properties of transition metal oxide based

materials thus necessitates comprehensive studies of their surface atomic and electronic structure. We use the combination of high resolution Scanning Tunneling Spectroscopy and Microscopy with first principles density functional calculations to elucidate the electronic and chemical properties of one dimensional defects on a $\text{TiO}_2(110)$ surface. Previously, Onish and Iwasawa reported that oxygen-deficient $\text{TiO}_2(110)$ regenerates its (1x1) surface of the bulk-like termination, via "added rows of Ti_2O_3 " [Phys. Rev. Lett. 76, (1996) 791]. We present a scanning tunneling microscopy/spectroscopy (STM/STS) study of the added rows on a reduced $\text{TiO}_2(110)$, clearly revealing their internal structure. High-resolution STM images show extra Ti atoms coordinated in sites of oxygen octahedral channels. In this re-oxidation scheme, these Ti atoms form edge-shared octahedra with five-fold Ti^{4+} on surface. The added structure is reminiscent to crystallographic shear planes, in which normally corner-shared octahedra in stoichiometric rutile TiO_2 slip to form face-sharing octahedra to remove the oxygen vacancies. This result provides a new paradigm for the defect chemistry of this surface. The adsorption of O_2 on defects is studied by in-situ STM, illustrating the role of these defects in a surface/gas-phase reaction on $\text{TiO}_2(110)$.

10:15 AM *R9.6/P6.6

Seeing Catalysts at Work at High Temperatures and High Pressures, Using STM. J. W. M. Frenken¹, B. L. M. Hendriksen¹, M. D. Ackermann¹, S. Bobaru¹, O. Robach², I. Popa², H. Kim² and S. Ferrer²; ¹Kamerlingh Onnes Laboratory, Leiden University, Leiden, Netherlands; ²European Synchrotron Radiation Facility (ESRF), Grenoble, France.

This talk discusses experiments performed with two complementary techniques, Scanning Tunneling Microscopy and Surface X-Ray Diffraction, investigating the relation between structure and chemical activity of model catalysts under semi-realistic working conditions. We use the so-called $\text{Re}^{\text{actor-STM}}$, a small STM that is integrated with a miniature, high-temperature (500 K), high-pressure (5 bar) reactor cell, inside an ultrahigh vacuum chamber. Reactive gas mixtures at atmospheric pressures flow over the investigated surface, while it is being imaged with the STM. Simultaneously with the imaging, the hot gas mixture, which leaves the reactor, is mass analyzed. Our SXRD experiments are performed in a combined UHV and high-pressure chamber, which can be operated as a batch reactor. Results will be shown for the oxidation of CO on Pt and Pd surfaces, which demonstrate that under high-pressure conditions the mechanism and kinetics for this important reaction are radically different from those in ultrahigh vacuum [1,2]. We resolve various ultrathin oxide structures, which only appear under high partial pressures of oxygen and on which the CO oxidation reaction proceeds via the so-called Mars-van-Krevelen mechanism, i.e. the extraction of oxygen atoms from the oxide. One of the oxide structures is found to be stabilized by the simultaneous presence of both O_2 and CO [3]. Finally, we have observed self-sustained oscillations in the reaction rate and we introduce a simple, new model for these oscillations, which is fully based on our STM and SXRD observations and does not rely on intrinsic non-linearities in the reaction rates. [1] B.L.M. Hendriksen and J.W.M. Frenken, Phys.Rev.Lett. 89 (2002) 046101. [2] B.L.M. Hendriksen, S.C. Bobaru, and J.W.M. Frenken, Surf.Sci. 552 (2004) 229. [3] M.D. Ackermann, O. Robach, B.L.M. Hendriksen, S. Bobaru, I. Popa, H. Kim, J.W.M. Frenken, and S. Ferrer, to be published.

10:45 AM R9.7/P6.7

Heterogeneous Photocatalysis of Oxidation of Acetaldehyde using Titania Nanotubes. Huifang Xu¹, Ganesh Vanamu², Ziming Nie¹, Jonathan Phillips³ and Yifeng Wang⁴; ¹Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin; ²Chemical and Nuclear, University of New Mexico, Albuquerque, New Mexico; ³Engineering Science and Applications Division, Los Alamos National Laboratories, Los Alamos, New Mexico; ⁴Sandia National Laboratories, Albuquerque, New Mexico.

This work shows that simple, standard methods of metal addition, without the need for ion implantation or other complex and expensive processes, can dramatically improve the performance of some titania structures for some (i.e. hydrocarbon oxidation) photocatalytic reactions. Titania nanotubes were prepared and incorporated with Au (Au/Nanotube sample) and Pt (Pt/Nanotube sample), and studied the photoactivity of these catalysts. These samples were compared with an industrial standard P25 (Degussa) photocatalyst. The samples were analyzed using a JEOL FEG-2010F field emission gun scanning transmission electron microscopy (STEM) with attached Oxford Instruments, X-ray energy-dispersive spectroscopy (EDS) system and Gatan imaging filtering (GIF) system. Both high-resolution TEM images and high angle dark-field (HAAD) images were recorded for the specimens. Titania nanotubes produced had a consistent structure, and highly dispersed metal catalysts. It was observed that the nanotube consists of low defect density nanotubes all of which have an inner diameter of ~ 6nm. The Au/Nanotube sample contained 1 nm Au nano-particles attached to the nanotube surfaces.

The HAAD image did not show visible Pt clusters on the nanotube surfaces. However, X-ray EDS spectra clearly showed the Pt in the nanotubes. It is inferred that Pt ions are distributed evenly on both outer and inner surfaces of the nanotubes. The white Pt/Nanotube sample turned grayish after the photocatalytic reaction. Oxidation of acetaldehyde was used to test the efficiency of the catalysts. Nanotube samples showed better photoactivity than the standard P25. Both the metal identity and the size of the metal particles in the nanotubes affected the photo-activity. Specifically, Pt containing nanotube was a dramatically better catalyst than P-25. The addition of gold had lesser impact compared to the platinum. Au/Nanotube sample showed more than twice the rate of the pure nanotube sample. Pt/Nanotube sample showed the highest rate, more than 10 times the rate of P25. This sample showed 6 times rate of the pure nanotube sample. It suggested that the nanotubes with uniformly distributed Pt (ions) are more photo-reactive than those with Pt nano-particles. Pt nano-particles formed on the nanotube surfaces reduced the reactivity oxidation. It was also found that the reactivity decreased with bigger size particles. The nanotube sample coated with about 2~3 nm (bigger size) Au and Pt nano-particles showed lower photo-reactive rates compared to the Au/nanotube and Pt/nanotube samples.

11:00 AM R9.8/P6.8

Ordered Arrays of Metal Nanoclusters on Oxide Surfaces. Guido Mariotto¹, Nikolai Berdunov¹, Shane Murphy¹, Kannan Balakrishnan¹, Yakob M. Mukovskii² and Igor V. Shvets¹; ¹Physics, Trinity College Dublin, Dublin, Leinster, Ireland; ²MISIS, Moscow, Russian Federation.

The metal-oxide interface is of fundamental importance in many areas such as microelectronics, corrosion and catalysis. Magnetite and iron play an important role in industrial processes such as the production of hydrogen and the synthesis of ammonia. The ability of controlling the size and arrangement of Fe nanostructures may influence the way catalytic processes take place. Furthermore, the self-assembly of ordered arrays of metal nanoclusters is a particularly promising subject for microelectronics and ultra-high density recording. We have studied the formation of Fe nanostructures on the magnetite (111) surface of single crystals and thin films. The $\text{Fe}_3\text{O}_4(111)$ surface exhibits an hexagonal 42 Å superstructure, when annealed in oxygen atmosphere [1]. We have shown that this highly regular pattern is useful as a template for the self-assembly of nanostructures. We have deposited Fe films of 0.2, 0.5, 1 and 2 Å thickness at room temperature by means of electron beam evaporation. STM images prove that ordered nucleation of nanoclusters takes place only on the patterned regions of the surface, while random nucleation takes place on the unpatterned regions. These results have been reproduced in the case of a 0.5 Å Cr film. The metal nanostructures are characterized by a very regular size distribution over a length of several hundreds nanometers. Our results demonstrate that the self-assembly of crystalline Fe and Cr nanostructures takes place on the preferential nucleation sites provided by the nanopatterned $\text{Fe}_3\text{O}_4(111)$ surface. We suggest that ordered arrays of nanostructures could be grown on different oxides displaying long-range surface reconstruction, as recently demonstrated by the growth of ordered Pd clusters on Al_2O_3 [2]. [1]. N. Berdunov, S. Murphy, G. Mariotto and I.V. Shvets, Phys. Rev. B 70, 085404 (2004). [2]. S. Degen, C. Becker and K. Wandelt, Faraday Discuss. 125, 343 (2004).

11:15 AM R9.9/P6.9

In situ Observation of Electrode Reactions on Solid Electrolytes Probed by Microspectroscopy. Bjoern Luerssen, Holger Fischer and Juergen Janek; Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany.

In-situ microspectroscopic investigations of metal (Pt) and oxide electrodes deposited on the ion conducting solid electrolyte YSZ (= yttria stabilized zirconia) contribute to the mechanistic understanding of the electrode processes under polarization conditions. In our experiments we use Photoelectron Emission Microscopy (PEEM) and Scanning Photoelectron Microscopy (SPEM) to investigate the behaviour of Platinum electrodes upon anodic and cathodic polarization and to obtain local chemical information about the electrode and the electrolyte material. Three different types of electrodes were used: porous Pt paste electrodes, microstructured electrodes and dense Pt electrodes prepared via pulsed laser deposition (PLD). The results upon anodic polarization show (in contrast to the literature [1]) the formation of normal chemisorbed oxygen on the platinum surface [2]. Upon cathodic polarization reduction fronts are observed at the surface of the solid electrolyte which are interpreted as a local increase of the electron concentration due to the reduction of zirconium dioxide [3]. This reduction is almost complete in the case of polycrystalline YSZ, i.e. Zr(0) species can be identified in the XPS spectra. The lowest oxidation state of the single crystalline samples is

(under our experimental conditions) Zr(1+). The dense electrodes allow the exact microscopic determination of the three phase boundary as the place of the oxygen evolution. For the first time, a surface reaction could be imaged with SPEM. The experimental results are presented together with mechanistic considerations on both the NEMCA effect (NEMCA = Non Faradaic Electrochemical Modification of Catalytic Activity) and the cathodic reduction of the solid electrolyte [4]. [1] S. Ladas, S. Kennou, S. Bebelis, C. G. Vayenas, J. Phys. Chem., 1993, 97, 8845 [2] B. Luerssen, S. Guenther, H. Marbach, M. Kiskinova, J. Janek, R. Imbihl, Chem. Phys. Lett., 2000, 316, 331 [3] B. Luerssen, J. Janek, R. Imbihl Solid State Ionics, 2001, 141-142, 701-707 [4] B. Luerssen, S. Guenther, M. Kiskinova, J. Janek, R. Imbihl Phys. Chem. Chem. Phys., 2002, 4, 2673-2679

11:30 AM R9.10/P6.10

In-situ Monitoring of Oxygen Spillover Ions on Pt/YSZ Electrodes. Juergen Janek¹, Bjoern Luerssen¹, Holger Fischer¹ and Sebastian Guenther²; ¹Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany; ²Department Chemie, Ludwig-Maximilians- Universitaet Muenchen, Muenchen, Germany.

In-situ microspectroscopic investigations of metal (Pt) and oxide electrodes deposited on the ion conducting solid electrolyte YSZ (= yttria stabilized zirconia) contribute to the mechanistic understanding of the processes at the three phase boundary and thus of the catalytic processes under polarization conditions [1]. The general aim of our studies is the control of catalytically active surfaces via ion-pumping in electrochemical cells. In our experiments we use Photoelectron Emission Microscopy (PEEM) and Scanning Photoelectron Microscopy (SPEM) to investigate the behaviour of platinum electrodes (prepared by pulsed laser deposition) during anodic polarization and to obtain local chemical information about the electrode and the electrolyte material. The SPEM allows two working modes: acquiring spectra (with an energy resolution of ca. 0.2 eV) or images (on a specific kinetic energy with a spatial resolution of approximately 500 nm). By this means it was possible to image the surface diffusion of oxygen spillover species in-situ by PEEM. As the diffusion process is too fast for a direct imaging in SPEM we chose an indirect way: Firstly, the electrode surface was covered with carbon. Afterwards, the polarization was started and the surface reaction $C + 2 O(ad) \rightarrow CO_2$ was imaged [2]. References: [1] C. G. Vayenas et al., Electrochemical Activation of Catalysis, Kluwer Academic/Plenum Publisher, New York 2001 [2] B. Luerssen, H. Fischer, J. Janek, S. Guenther, In Situ Microspectroscopy of Polarized Pt/YSZ Electrodes, in: Solid State Ionics: The Science and Technology of Ions in Motion, World Scientific, Singapore 2004, pp. 139-149

SESSION R10: Synthesis of Nanoporous Materials I
Chair: Witold Lojkowski
Thursday Afternoon, March 31, 2005
Room 3001 (Moscone West)

1:30 PM *R10.1

Carbide-Derived Carbon with Tunable Pore Size. Yury Gogotsi, Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Control over the material structure on nanoscale can open opportunities for the development of materials with superior properties, if the structure/property relations are known. This presentation is an overview of a new approach to synthesis of nanoporous carbons. Extraction of metals from carbides can produce a broad range of potentially important carbon nanostructures, which range from diamond to carbon onions and nanotubes [1-4]. For example, extraction of silicon, aluminum or titanium from their carbides results in the formation of ordered and disordered graphite and nanoporous carbon with specific surface area of 1000-2000 m²/g. This technology allows the control of carbon growth on the atomic level, monolayer by monolayer. Therefore, porosity of these carbons can be tuned with sub-Angstrom accuracy in the 0.5-2 nm range [3]. The structure of the carbon is controlled by the structure of the carbide precursor as well as process parameters including temperature, time and environment. The carbide-derived carbons (CDC) with a narrow pore size distribution and a large pore volume of 50-80% can be used for gas storage, separation, catalysis and other applications. 1. Nikitin, Y. Gogotsi, Nanostructured Carbide-Derived Carbon (CDC), in Encyclopedia of Nanoscience and Nanotechnology, H.S. Nalwa, Ed., v. 7, pp. 553-574 (American Scientific Publishers, CA 2003) 2. Y.G. Gogotsi, M. Yoshimura, Formation of Carbon Films on Carbides under Hydrothermal Conditions, Nature, v. 367, 628-630 (1994) 3. Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J.E. Fischer, B. Yi, H.C. Foley, M.W. Barsoum, Nanoporous Carbide-Derived Carbon with Tunable Pore Size, Nature Materials, v. 2 (9) 591-594 (2003) 4. Y. Gogotsi, S. Welz, D.A. Ersoy, M.J. McNallan, Conversion of Silicon Carbide to Crystalline Diamond-Structured Carbon at Ambient

Pressure, Nature, v. 411, 283-287 (2001)

2:00 PM R10.2

Nanoporous Carbide-Derived Carbon for Potential Use in Water Purification and Gas Separation. Elizabeth N. Hoffman, Gleb Yushin, Michel W. Barsoum and Yury Gogotsi; Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Recently nanoscale tunable porosity was achieved by the chlorination of Ti₃SiC₂, a machinable ternary carbide that belongs to the M_{N+1}AX_N phase class of solids. In this work we extend the study to other carbide-derived carbons, CDCs, synthesized by the chlorination of other MAX solids such as Ti₂AlC. X-ray diffraction, Raman spectroscopy, HRTEM, and sorption analysis of CDC obtained from the chlorination of Ti₂AlC and other MAX phases in the 400 to 1200 °C temperature range confirmed a structural dependence on chlorination temperature. At low chlorination temperatures, the CDC structure appears primarily amorphous. As the chlorination temperature increases, graphitic ribbons form. In addition to increased graphitization, increasing the chlorination temperature resulted in an increased average pore size. With proper chlorination temperature and initial starting ternary carbide phase, the resulting CDC pore size distribution is narrower than single-walled nanotubes and comparable to zeolites. Preliminary results show that these CDCs with their narrow nanopore size distribution, along with their tunability, show tremendous potential in applications such as water purification, hydrogen storage and gas separation applications. * Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J.E. Fischer, B. Yi, H.C. Foley, M. W. Barsoum, Nature Materials 2 (2003) 591-594.

2:15 PM R10.3

Metal Incorporation into Nanoporous Carbon. Simon John Henley, J. D. Carey and S. R. P. Silva; Advanced Technology Institute, University of Surrey, Guildford, Surrey, United Kingdom.

Nanoporous carbon films were deposited by 248 nm pulsed laser ablation of a graphite target in different background pressures of argon (P_{A,r}). The morphology changed from smooth, high-density amorphous carbon films at P_{A,r} = 20 mTorr to ultra-low density nanoporous material at P_{A,r} = 400 mTorr. Here the nanostructural, chemical and electrical properties of metal containing nanoporous carbon samples are investigated by ablating graphite targets containing known contents of different metals such as Ni and Co. We demonstrate how the ablation plume dynamics affect both the nanostructure of the material and the incorporation of metal atoms. The suitability of these functionalised ultra-low density materials for gas sensing and energy storage applications will be discussed.

2:30 PM R10.4

Nanoporous and Nanostructured Materials Made out of Clusters for Environmental Applications. Jiji Antony¹, You Qiang¹, Amit Sharma¹, Nutting Joe¹, Chongmin Wang², Donald R. Baer², David E. McCready², Mark Engelhard², James T. Nurmi³ and Paul Tratnyek³; ¹Physics, University of Idaho, Moscow, Idaho; ²EMSL, Pacific Northwest Laboratory, Richland, Washington; ³Environmental and Biomolecular Systems, Oregon Health and Science University, Portland, Oregon.

Metallic iron is used to chemically reduce contaminants, such as chlorinated hydrocarbons, for environmental cleanup. The use of nano-sized particles of iron is of interest because of enhanced possibilities for distribution, a high rate of reactivity and the possibility enhancing environmentally friendly reaction paths. Iron-iron oxide core shell nanoclusters are of great interest due to its potential application as a remedy for the environmental contamination. An oxide shell or other protective layer Oxide shells plays an important role along with the metallic iron core in chemical reactions. Those core-shell nanoclusters promotes the reduction of chlorinated hydrocarbons, a major source of environmental contamination. The Examination of the chemical properties of synthesis of monodisperse metallic iron nanoparticles with a well-defined clean oxide shells is important to understand the chemistry of nanoparticles. However, production of these particles by conventional methods is difficult. Therefore and hence we developed are using a cluster deposition system, which prepare the iron nanoclusters and iron-iron oxide core shell nanoclusters at room temperature by a method that is a combination of high-pressure sputtering and aggregation techniques. For this we used a 3inch diameter by 3mm thick iron target of 3N purity and sputter it with Ar ions. The Fe nanoclusters are formed by the aggregation of these Fe atoms. Clusters then move into an oxygen rich atmosphere in the deposition chamber and core shell structures are developed. These clusters are then deposited onto a substrate placed on the substrate holder, which is transferred into the deposition chamber using a load-lock system. The core shell structure can be also formed when the metallic iron nanoclusters are taken out of the deposition chamber

and gets oxidized naturally in atmosphere. In this iron iron-oxide core shell nanoclusters, the outer oxide layer acts as a passivation layer preventing further oxidation of the cores upon continued exposure to the atmosphere. Size of the iron-iron oxide core-shell nanoclusters can be varied with the rate of He and Ar gas flows, the chamber pressure, the sputtering power and the growth distance. Cluster films are characterized by XPS, XRD, HRTEM and voltametry measurements. The bcc nanocrystalline iron core is observed by XRD. The selected area diffraction and the nano-beam diffraction measurements by HRTEM also revealed the bcc crystal structure. We still found the core-shell structures in the samples measured by TEM months later, which indicate that the core-shell nanostructured clusters are pretty stable. Voltametry measurement has confirmed the presence of metallic iron core and magnetite shells. Nanoporosity has been calculated and measured by BET.

2:45 PM R10.5

Electrodeposition of Nanoscale Semiconductors and Metals in Ionic Liquids. Frank Endres, Technical University of Clausthal, Institute of Metallurgy, Clausthal-Zellerfeld, Germany.

Ionic liquids are a new class of solvents with extraordinary physical properties. They are mostly based on organic cations and inorganic or organic anions and by definition their melting points are below 100 Celsius. These liquids have often negligible vapor pressure, high thermal stability (up to 350 Celsius), high ionic conductivity and wide electrochemical windows of up to 7 Volt. The latter property is very important for the electrodeposition of reactive elements such as Ge, Si, Al, Li and many others. We could show by the help of the in situ Scanning Tunneling Microscope that the initial processes of germanium and silicon electrodeposition can be probed on the nanometer scale. For example, before the bulk phase of germanium forms, an underpotential deposition sets in, and ultrathin layers between 100 and 300 pm with clearly metallic behavior grow [1-3]. With subsequent reduction nanocrystallites start growing that show a metal to semiconductor transition in the thickness regime between 1 and 10 nm. With these liquids it is also possible to electrodeposit silicon, and we could show by in situ tunneling spectroscopy that a 100 nm thick silicon film has a band gap of 1.0 \pm 0.1 eV, proving that intrinsic semiconducting silicon was electrodeposited [4]. Thin nanoscale layers of silicon can be prepared easily. Such ionic liquids are also well suited to the electrodeposition of nanocrystalline metals and alloys. We could show that aluminum can be made as bulk samples with grain sizes down to 10 nm. Furthermore nanocrystalline noble metals like Palladium can be made with crystal sizes below 50 nm [5]. Metallic selenium, an important element for diodes and photovoltaic cells, can be made easily in ionic liquids at elevated temperature. In the anodic regime it is possible to electropolymerize benzene, and as a result one gets nanoporous polyphenylene, which could be interesting for Organic Light Emitting Diodes [6]. In this paper an overview on the electrodeposition of nanocrystalline metals and semiconductors as well as on nanoporous polymers shall be given. [1] F. Endres, S. Zein El Abedin, Phys. Chem. Chem. Phys., 4 (2002) 1640 [2] F. Endres, S. Zein El Abedin, Phys. Chem. Chem. Phys., 4 (2002) 1649 [3] F. Endres, S. Zein El Abedin, Phys. Chem. Comm 8 (2002) 892 [4] S. Zein El Abedin, N. Borissenko, F. Endres, Electrochemistry Communications, 6 (2004) 510 [5] F. Endres, M. Bukowski, R. Hempelmann, H. Natter, Angew. Chemie, Int. Ed., 42 (2003) 3428 [6] S. Zein El Abedin, N. Borissenko, F. Endres, Electrochemistry Communications, 6 (2004) 422

3:15 PM *R10.6

Mesoporous Nanostructured Architectures for High Performance in Rate-Critical Applications. Debra R. Rolison¹, Jeffrey W. Long¹, Michael S. Doescher¹, Jeremy J. Pietron¹, Michael S. Logan¹, Everett E. Carpenter², Christopher P. Rhodes¹ and Rhonda M. Stroud²; ¹Surface Chemistry Branch, Naval Research Laboratory, Washington, District of Columbia; ²Materials and Sensors Branch, Naval Research Laboratory, Washington, District of Columbia.

Sensing, catalysis, and magnetic separations 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, low density, ultraporous nanoarchitectures, conjoin high surface area for heterogeneous reactions with a continuous, porous network for rapid diffusional flux of molecules. In MnO₂ ambigels with <20-nm pores, proton wires with macroscopic lengths form upon exposure to humid atmospheres as water layers adsorb at the solid framework. The increased electrical conductivity conferred by this monolithic proton wire improves the sensitivity factor for humidity by 14-fold relative to particulate films of MnO₂. 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. Composite aerogels prepared by nanogluing ligand-stabilized gold nanoparticles with titania sol exhibit enhanced catalytic activity for

room-temperature oxidation of carbon monoxide and do so with nominally inactive (5.5 nm) Au particles. The high activity arises from multiple titania-gold junctions that inherently form during aerogel synthesis and processing [2]. Ligand-stabilized guests in aerogel hosts may offer a general means to improve interfacial contact between nanoparticulate catalysts and nanostructured, activating supports. Superparamagnetic mesoporous aerogels of magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) are monolithic, tailorable nanoarchitectures that offer an advanced form of reactive membrane for magnetic separations. [1] D.R. Rolison, Science 299 (2003) 1698. [2] J.J. Pietron, R.M. Stroud, D.R. Rolison, Nano Lett. 2 (2002) 545.

3:45 PM R10.7

Palladium-Polyimide Nanocomposite Membranes: Synthesis and Characterization of Reflective and Electrically Conductive Surface Metallized Films. Luke M. Davis¹, B. L. French³, David Wallace Thompson¹ and Robin E. Southward²;

¹Chemistry, College of William and Mary, Williamsburg, Virginia; ²Advanced Materials and Processing Branch, NASA, Langley Research Center, Hampton, Virginia; ³Applied Science, College of William and Mary, Williamsburg, Virginia.

Palladium surface-metallized polyimide films were prepared by an unusual macromolecular matrix mediated, single stage synthetic protocol first reported by Taylor et al. (J.A.C.S. 1980, 102, 876). Several Pd(II) complexes, [PdCl₂(SMe₂)₂], [PdBr₂(SMe₂)₂], and Pd(CF₃COO)₂ were dissolved in the poly(amic acids of BTDA/ODA and BPDA/ODA in the solvent DMAc. Films cast onto glass plates from these Pd(II)-doped resins were thermally cured to 300 C in air which resulted in air-side surface-metallized membranes. The films were characterized by both specular and diffuse reflectivity and by conductivity measurements as a function of the cure time and temperature. Maximum specular reflectivities of ca. 50% were observed at 530 nm. After achieving maximum specular reflectivities in the thermal cure cycle at 300 C from 0.5-2 h, the film surface quickly degraded upon further curing. The surface sheet resistivities were in the range 1-50 ohm/square. Initial Pd metal particles formed in the film were in the 3-10 nm range. The optical data coupled SEM micrographs, elemental analytical results, and X-ray diffraction observations were interpreted to support a mechanism for the formation of a reflective and conductive metallized surface which involves selective air-side surface oxidative degradation of the polyimide matrix to volatile products which then concentrates the metal nanoparticles at the surface and increases particle size via sintering. The mechanical properties of the metallized films are compromised with respect to the parent polyimide although the composite membranes are still useful for a range of applications, particularly if one begins with relatively thick poly(amic acid) precursor films. The tensile strength is reduced; the percent elongation and the tensile modulus are increased. Both BTDA/ODA and BPDA/ODA gave very similar results with the Pd(II) additives. Interestingly, many Pd(II) compounds, e.g., PdBr₂, were not useful in generating a metallized surface which suggests that the pathway to a metallized surface is extremely sensitive to experimental conditions.

4:00 PM R10.8

Prepatterning of Substrates via Diblock Copolymer Lithography. Danilo Zschech¹, Dong Ha Kim², Alexey P. Milenin¹, Martin Steinhart¹ and Ulrich Goesele¹; ¹Max Planck Institute of Microstructure Physics, Halle, Germany; ²Max Planck Institute for Polymer Research, Mainz, Germany.

Porous materials have attracted increasing interest particularly in nanotechnology. Examples are their application as templates for the synthesis of one-dimensional nanostructures, and as highly selective membranes for separation applications (1). Prerequisites for this are a uniform pore size distribution, a regular arrangement of the pores, and the possibility to prepare laterally extended, continuous porous films. A simple and versatile method to prepare such porous structures characterized by lattice constants of a few tens of nanometers is based on self-assembly of diblock copolymers (2,3). Compared to electron beam lithography, this approach allows the patterning of large areas (up to several cm²) at considerably lower cost. Further benefits are the easy tailoring of the lattice constant by properly adjusting the molecular weight of the used block-copolymer and its self-healing behaviour. Thin films of polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) on various substrates consisting of cylindrical domains of the minor phase PMMA oriented normal to the film plane were prepared by spin-casting and annealing under inert atmosphere. After exposing to UV light followed by rinsing in acetic acid an ordered holey film of polystyrene was obtained and used for lithography (4). We employed reactive ion etching (RIE) to transfer the pattern into the underlying substrates. To enhance the etch contrast, the major phase consisting of the styrene blocks may be stained with ruthenium tetroxide. The thus patterned substrates can be further processed to obtain extended, highly ordered porous materials with pores having high aspect ratios. Such porous materials may be used as nanosieves,

high temperature-resistant lithographic masks for the growth of nanowires or for subsequent electro-chemical etching processes. (1) M. Lazzari, M. Lopez-Quintela, *Advanced Materials*, 2003, 15, 1583. (2) K. Guarini, C. Black, S. Yeung, *Advanced Materials*, 2002, 14, 1290. (3) P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* 1997, 275, 1458. (4) C. Black, K. Guarini, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2004, 42, 1970.

4:15 PM R10.9

Direct Synthesis of Mesoporous Carbon and Palladium-Containing Mesoporous Carbon With Tunable Pore Size. Qingyuan Hu, Jiebin Pang, Zhiwang Wu and Yunfeng Lu; Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana.

Activated carbon supported catalysts are commonly used in organic synthesis and fine chemical industry, however, they are typically microporous with broad pore size distributions, which may limit their catalytic applications involve large size organic molecules. Mesoporous carbon materials may overcome this obstacle since they contain larger pore sizes, narrow pore size distributions, higher surface areas and larger pore volumes. In recent years, there has been a great interest in the synthesis of mesoporous carbons due to their attractive characteristics. To date, various mesoporous carbon materials have recently been synthesized using preformed mesoporous silica as template which is experiencing difficulties in pore size control. In this study, we demonstrate a direct-template technique to fabricate mesoporous carbon with high surface areas, narrow and tunable pore size distributions and large pore volumes. This is achieved by coassembly of carbon precursors and silicate species through a simple sol-gel process. Carbonization and sequent template removal leads to the formation of mesoporous carbon with controlled pore dimensions. The pore diameters of the mesoporous carbon can be adjusted from about 2 nm to more than 10 nm by changing synthesis condition. Such materials are ideal for catalyst supports and other applications. For example, palladium-containing mesoporous carbon materials with different pore size were synthesized. The effects of pore size on the catalytic performance were also tested.

4:30 PM R10.10

Formation, Characterization, and Efficient Direct Nitridation of Unique ZrO_x and HfO_x Nanostructures and their Composites with TiO_x . James L. Gole¹, Sharka M. Prokes², John D. Stout¹ and Orus J. Glembocki²; ¹School of Physics, Georgia Institute of Technology, Atlanta, Georgia; ²Naval Research Lab, Washington, District of Columbia.

ZrO_2 and HfO_2 nanoparticles and nanostructures have been synthesized in a variety of forms from the oxidation of the chloride and oxychloride at temperatures ranging from 300 to 450 degrees C. A modified flow-tube furnace configuration carefully calibrated for temperature, temperature gradients, entrainment gas flow rate and oxidant seeding, and total pressure has allowed a considerable variation in product formation. Under certain experimental conditions, small semiporous metal oxide nanoparticles of diameter 20-80 nm are formed and can be converted to the oxynitride by treatment with alkyl ammonium compounds. They can be placed in solution to form slurries that allow the subsequent formation of metal oxide and oxynitride films. We report the first synthesis of unique zirconia-based nanoshells and hollow nanospheres. These materials have been studied using a combination of transmission electron microscopy, Raman, and Photoluminescence spectroscopy. The formation of the nanoshells and nanospheres can be made to dominate the formation of other less defined solid but porous zirconia-based nanostructures under select experimental conditions. The hollow ZrO_x nanospheres (and nanoshells) are of diameter 20-250 nm and wall thickness 5-20 nm. In contrast to zirconia-based nanoparticles and nanospheres, we find that the nanoshell configurations demonstrate a significantly enhanced photoluminescence. The focusing properties* inherent to the nanoshell paraboloids are suggested to be responsible for their greatly enhanced photoluminescence (~60X) compared to that of either nanospheres or other less-defined nanoparticle agglomerates. The potential applications of these nanospheres as lightweight replacements for carbon black in automobile tires to hydrogen storage are being evaluated using density measurements and a Sievert's analysis of the hydrogen uptake. In contrast to results from micron-based studies, we have been able to readily produce ZrO_2/TiO_2 nanostructure composites that can be made to range in composition across a wide range of composition. Both titanium and zirconium oxide are Lewis acid catalysts, with TiO_2 being the stronger Lewis acid. Zirconia and to a lesser extent, TiO_2 , have been converted into much stronger acids by the addition of sulfuric acid to the solids. With this change, the sulfated oxides demonstrate both strong Lewis and Bronsted acidity. The ability to form a solid solution of these two raises the question of how their strong acidity can be tuned by changing the composition of the solid. The results of our studies of these systems will be reported.

4:45 PM R10.11

Atomic Layer Deposition of ZnO on Ultra-Low-Density Nanoporous Silica Aerogel Monoliths. S. O. Kucheyev¹, J.

Biener¹, Y. M. Wang¹, T. F. Baumann¹, K. J. Wu¹, T. van Buuren¹, J. H. Satcher¹, J. F. Poco¹, A. V. Hamza¹, J. W. Elam² and M. J. Pellin²; ¹Lawrence Livermore National Laboratory, Livermore, California; ²Argonne National Laboratory, Argonne, Illinois.

Recent advancements in the sol-gel technology have led to a successful synthesis of a range of metal oxide aerogels including oxides of Ti, V, Cr, Fe, Sn, and Ru. However, some metal-oxide systems, such as ZnO, are currently not amenable to the sol-gel method used to synthesize aerogels. In this presentation, we demonstrate atomic layer deposition (ALD) of an ~2-nm-thick ZnO layer on the inner surface of ultra-low-density (~0.5% of the full density) nanoporous silica aerogel monoliths with an extremely large effective aspect ratio of ~10⁷ (defined as the ratio of the monolith thickness to the average pore size). The resultant monoliths are formed by amorphous-SiO₂/wurtzite-ZnO nanoparticles which are randomly oriented and interconnected into an open-cell network with an apparent density of ~3% and a surface area of ~100 m² g⁻¹. Secondary ion mass spectrometry and high-resolution transmission electron microscopy imaging reveal excellent uniformity and crystallinity of ZnO coating. Oxygen K-edge and Zn L₃-edge soft x-ray absorption near-edge structure spectroscopy shows broadened O 2p- as well as Zn 4s-, 5s-, and 3d-projected densities of states in the conduction band. This study demonstrates that ALD is a very attractive tool for the fabrication of novel monolayer catalysts and gas sensors based on well-developed, robust nanoporous monolithic material systems such as silica, alumina, and carbon aerogels. 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.

SESSION R11: Optical Properties and Photovoltaics

Chair: Ulrich Goesele

Friday Morning, April 1, 2005

Room 2009 (Moscone West)

8:00 AM R11.1

ZnO Nanowire Dye Sensitized Solar Cells. Jason B. Baxter and Eray S. Aydil; Dept. of Chemical Engineering, University of California Santa Barbara, Santa Barbara, California.

Dye sensitized solar cells (DSSCs) rely on light absorption by a monolayer of dye molecules adsorbed at the surface of a nanostructured wide band gap semiconductor, such as TiO₂, which is infiltrated by an electrolyte. Photoexcited electrons are rapidly transferred to the semiconductor conduction band and the dye is regenerated through a redox reaction with a redox couple in the electrolyte. Replacing the TiO₂ nanoparticles with a dense network of nanowires may be advantageous because the nanowire morphology provides direct conduction paths for the electrons from the point of injection to the collection electrode while maintain high surface area for dye adsorption. We have built DSSCs which employ single crystal ZnO nanowires as the dye support and electron transport medium. Solar cell characteristics depend on the nanowire morphology. To date the best nanowire based DSSCs exhibited energy conversion efficiencies of 0.5% with internal quantum efficiencies of 70%. ZnO nanowires were grown by metalorganic chemical vapor deposition (MOCVD) using zinc acetylacetonate ($Zn(acac)_2$) as the precursor in the presence of oxygen at 550 °C. Nanowires nucleate and grow spontaneously without catalysts or templates to seed the growth. Nanowire morphology can be varied from sparse, smooth nanowires to higher surface area dendrite-like nanostructures by changing the deposition conditions and deposition time. Nanowires ~80 nm in diameter and several microns long grow on various substrates including F:SnO₂, glass, and sapphire. Current-voltage characteristics of DSSCs constructed using these low surface area smooth nanowires showed the characteristic rectification expected of a photovoltaic device, but with short circuit currents under 10 $\mu A/cm^2$ and efficiencies of less than 0.001%. After longer times, secondary nanowires nucleate and grow from the primary nanowire backbone, increasing surface area significantly and resulting in currents up to 100 $\mu A/cm^2$ and efficiencies of 0.02%. Furthermore by replacing the $Zn(acac)_2$ precursor and continuing growth, we have formed branched dendrite-like nanostructures, greatly increasing the surface area for dye adsorption and improving the solar cell performance with each successive growth cycle. DSSCs using fourth generation dendritic nanowires have short circuit currents of 1.6 mA/cm², open circuit voltages of 0.71 V, overall efficiencies of 0.5%, and internal quantum efficiencies of 70%. Light harvesting efficiency is still less than 10% even with fourth generation nanowires, indicating that substantial gains in photocurrent can be made by further increasing nanowire surface area. By filling the interstitial spaces between nanowires with nanoparticles, we have combined the large surface area provided by nanoparticles with improved transport provided by nanowires. The

hybrid DSSCs have larger photocurrents than nanowire based devices and larger photovoltages than nanoparticle based cells.

8:15 AM R11.2

Unusual Optical Properties of Large Surface Area Nanoparticles - The First White-Light Nanophosphor.

Jess Patrick Wilcoxon, Billie Abrams, Steven Thoma and Paula Provencio; 1126, Sandia National Laboratories, Albuquerque, New Mexico.

We describe the synthesis and optical properties of a new class of extremely small, $d < 2.0$ nm, II-VI semiconductor quantum dots (QD) whose photoluminescence (PL) properties are controlled by their interfacial chemistry and age-dependent surface reconstruction. We demonstrate a decoupling of the absorbing states determined by quantum confinement, (the band-edge), from the emission states which are determined primarily by the interfacial states. This decoupling allows PL emission from a single size QD to be tuned throughout the visible range by surface chemistry, while eliminating the problem of self-absorbance of the emitted light. We demonstrate for the first time efficient, white light emission from a single material type, monodisperse nanosize phosphor. This discovery enables applications such as white LEDs based upon near-UV LEDs. The principles determining the optical properties of these new phosphors should extend to other nanosize semiconductors like Si and thus these new nanomaterials have great potential as white phosphors for solid-state and fluorescent illumination. Time permitting, we will also describe the synthesis and surface modifications of NIR emitting PbS and PbSe nanocrystals with 300 times the output power of the best NIR dyes at 1.1 and 1.5 μm . Acknowledgement: This work was supported by the Division of Materials Sciences, Office of Basic Energy Research, US Department of Energy under contract DE-AC04-94AL8500. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the US Department of Energy.

8:30 AM R11.3

Photonic and Optoelectronic Properties of a Nanoporous Cadmium Telluride based Metamaterial.

David Smith¹, Matthew L. Markham¹, Jeremy J. Baumberg¹, Xiaohong Li², Tim Gabriel², Iris Nandhakumar² and George S. Attard²; ¹School of Physics and Astronomy, University of Southampton, Southampton, Hampshire, United Kingdom; ²School of Chemistry, University of Southampton, Southampton, Hampshire, United Kingdom.

In this paper we will present experimental and theoretical investigations of the optical and optoelectronic properties of a nanoporous CdTe based metamaterial [1] closely related to mesoporous silica [2]. In particular we have fully characterised the nanostructuring induced birefringence [3] in these films and will present a theoretical model which fully explains the observed birefringence. We will also present the results of photocurrent spectroscopy and electrical impedance measurements which allow us to quantify charge transport within the films and the density and nature of surface states. The properties of this metamaterial indicates that it may find a wide range of applications from photovoltaics and photochemical catalysed reactions to phase-matched non-linear optical frequency mixing and in ultrafast photodiodes. The metamaterial is produced by electrochemical templating through a lyotropic liquid crystal template producing a thin film, 0.1-1 microns, of semiconductor containing a regular hexagonal array of cylindrical pores (diameter 3nm, separation 6nm). These films show strong negative uniaxial form birefringence, $\sim 4\%$, which we have fully characterised both above and below the semiconductor bandgap, in the spectral range 0.45-2 microns using polarised micro-reflectivity measurements. We have modelled the dielectric response expected from the measured morphology in the long wavelength limit using numerical finite difference and boundary integral approaches and also developed an approximate analytic solution. The three models give identical results. Using the modelled dielectric coefficient we have predicted the optical reflectivity of the samples and obtained a remarkable fit with experiments. As the birefringence of the films is dependent on the angle of the pores relative to the film normal this work may provide a means of better characterising a range of nanoporous films. The boundary integral model is extremely flexible, fast and easy to implement and so it is also likely to find wider applications. Whilst nanoporous materials have been tried in photovoltaic applications, mostly as electrodes in photochemical cells, and there have been some fundamental investigations of their charge transport properties [4], there is still much to be understood. In particular as even at very high doping levels the average spacing between dopants and the screening length are much greater than the pore separation it is not clear what role electric fields play in the transport of photoexcited charge. We will present comprehensive photocurrent and electrical impedance measurements of nanoporous CdTe-aqueous NaSO₃ Schottky diodes and discuss what can be learnt about surface states, charge transport and the doping of nanoporous

CdTe from these measurements. [1] I. Nandhakumar et al. Chem. Comm. 12 (2004) 1374 [2] G.S. Attard et al. Nature 378 (1995) 366 [3] M. Markham et al APL submitted [4] A. Hagfeldt et al. J. Phys. Chem. 100 (1996) 8045

8:45 AM R11.4

Luminescence of ZnO and ZrO₂ Nanopowders as Function of Grain Size and Method of Preparation. Larisa Grigorieva², Donats Millers², Agnieszka Opalinska¹, Roman Pielaszek¹, Tomasz Strachowski¹, Witold Lojkowski¹, Dariusz Hreniak³ and Wieslaw Strek³; ¹Institute for High Pressure Physics, Warsaw, Poland; ²Institute of Solid State Physics, University of Latvia, Riga, Latvia; ³Institute for Low Temperature and Structural Research, Polish Academy of Science, Wroclaw, Poland.

Luminescent oxides are used to detect ionizing radiation, for instance in scintillators used in medical devices. They are used also as phosphors in many applications. On the other hand, nanopowders made of oxides are extensively studied as material for gas sensors, where the small grain size contributes to sensitivity at relatively low temperatures. In that respect, nano-oxides can be regarded as multifunctional materials, where it is not excluded that various properties can be combined in one device. We studied luminescence of ZnO and ZrO₂ nanopowders as a function of grain size and method of preparation. The powders were synthesised in microwave driven hydrothermal process, under pressures up to 12 MPa. ZrO₂ powders with grain size in the range 7 - 15 nm have been produced starting from ZrOCl₂ aqueous solutions. The solutions were neutralized with NaOH to pH 10. Zirconia grain growth to 100 nm was stimulated by annealing in air. Zinc oxide was prepared from a zinc chloride (0.1M) solution alkalinized by KOH to pH value 10 or with the addition of urea in (1:1, 1:2, 1:3, 1:4 and 1:5) weight ratio to zinc chloride. The powders were thoroughly investigated by a range of methods. In particular, the grain size distribution was determined using a novel method of XRD line profile analysis. Fourier Transform Infrared Spectroscopy (FTIR) supported our research on the effect of surface state on luminescence. As far as ZrO₂ (both doped with rare earth ion Pr, and undoped) is concerned, we observed a strong dependence of luminescence decay time depending on the grain size of the powders. The increase of luminescence decay was observed with increasing grain size. This result again shows that the surface related defects strongly influence luminescence. ZnO due to the fast decay time of luminescence (in the 1 - 10 nm range) is a good candidate material for scintillators used in medical applications. For ZnO, depending on the synthesis conditions, both a yellow (1.5 - 2.2 eV) and blue (3.32 eV) luminescence band, or only the blue luminescence band were observed. The yellow luminescence is attributed to emission from defects. Since it can be eliminated in nanopowders using specific synthesis conditions, it follows that the defects are situated mainly on the surfaces of the nano-powders. This suggestion is supported by FTIR investigations, that shows that fractions of chemicals used in synthesis process could be found as impurities in nanopowders and different absorption spectra are observed depending on the synthesis reaction. Further studies are in course in order to identify the mechanisms of luminescence as a function of grain size, method of preparation, and conditions of the experiment. However, the engineering of the nanopowders luminescence is possible by using appropriate organic molecules for covering the nanopowder surface.

9:00 AM R11.5

Dye-sensitization of Tin Dioxide via the Functionalization of Oxide Surfaces with Organotrialkynyltins.

Thierry Toupance¹, Bernard Jousseau¹, Mervyn de Borniol¹, Hubert Cachet² and Vincent Vivier²; ¹Laboratory of Organic and Organometallic Chemistry LCOO UMR 5802, University of Bordeaux 1, Talence, France; ²Laboratoire des Interfaces et Systemes Electrochimiques, LISE UPR 15 CNRS, CNRS, Paris, France.

Efficient light-to-electricity conversion can be achieved with DSSC based on semiconducting oxides, such as titanium dioxide, sensitized with ruthenium polypyridyl complexes endowed with carboxylic acid moieties [1]. Compared to TiO₂, tin dioxide is a better electron acceptor owing to its more positive conduction band edge and the corresponding devices exhibit better long-term stability under UV-light due to its larger band gap. Nonetheless, the adsorption of dyes bearing carboxylic acid groups onto SnO₂ surfaces is very poor which drastically affects the efficiency of the related cells. Consequently, new strategies have to be developed to modify SnO₂ surfaces in order to exploit both fundamental and practical advantages offered by this oxide. Our group has recently shown that organotrialkynyltins were versatile precursors of SnO₂-based hybrid materials [2]. It would be therefore worthwhile to use these molecules as dye precursors to anchor strongly an organic dye onto SnO₂ nanoporous materials via the formation of a stable Sn(oxide)-O-Sn-C(alkyl) linkage. We herein report on the synthesis of perylene-3 or perylene-3,4-dicarboximide-substituted trialkynyltins from the suitable aryl bromide. These dye precursors react with

nanoporous SnO₂ powders or films to give photoresponsive hybrid materials which are stable in organic and aqueous media. The characterization and the photoelectrochemical behaviour of these materials will be discussed [4]. [1] Nazeeruddin, M.K.; Pechy, P.; Renouard, T.; Zakeeruddin, S.M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Sklover, V.; Spiccia, L.; Deacon, G.B.; Bigozzi, C.A.; Gratzel, M. *J. Am. Chem. Soc.* **123** (2001) 1613. [2] Elhamzaoui, H.; Jousseume, B.; Riague, H.; Toupance, T.; Dieudonne, P.; Zakri, C.; Maugey, M.; Allouchi, H. *J. Am. Chem. Soc.* **126** (2004) 8130. [3] Vilaca, G.; Barathieu, K.; Jousseume, B.; Toupance, T.; Allouchi, H. *Organometallics* **22** (2003) 4584. [4] a) Cachet, H.; Vivier, V.; Toupance, T. *J. Electroanal. Chem.* **572** (2004) 249. b) Han, C-W.; Jousseume, B.; Rasle, M-C.; Toupance, T.; Cachet, H.; Vivier, V. *J. Fluorine Chem.* **125** (2004) 1247.

9:15 AM R11.6

Fluorescent Silica Nanotubes Prepared by The Sol-Gel Template Method and Their Application in Gene Delivery. Yi-Hsin Liu¹, Yao-Chung Liu¹, Chia-Hsuan Wu¹, Chun-Chia Yeh¹, Ming-Tsan Su³, Yi-Chun Wu^{4,5} and Chia-Chun Chen^{1,2}; ¹Chemistry, National Taiwan Normal University, Taipei, Taiwan; ²Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan; ³Life Science, National Taiwan Normal University, Taipei, Taiwan; ⁴Life Science, National Taiwan University, Taipei, Taiwan; ⁵Institute of Molecular and Cellular Biology, National Taiwan University, Taipei, Taiwan.

Silicon dioxide nanotubes with diameters of hundred nanometers are synthesized using sol-gel deposition method with anodic aluminum oxide membrane (AAO) as nanoporous template. Green and red fluorescent silica nanotubes are made by modifying the inner side of the nanotubes with semiconductor nanocrystals. The localization of nanotubes within the cells is monitored using fluorescent microscopy. Furthermore, the fluorescent silica nanotubes are used to carry enhanced green fluorescence protein (EGFP) DNA into COS-7 cells. Expression of fluorescent proteins in COS-7 cells suggests that these silica nanotubes potentially be engineered into gene delivery vehicles. More biological applications of silica nanotubes will be also discussed.

9:30 AM R11.7

Synthesis and Characterization of Tin Nanoclusters. Billie Lynn Abrams, Jess P. Wilcoxon, Steven G. Thoma and Paula Provencio; Sandia National Laboratories, Albuquerque, New Mexico.

When the diameter of a nanocluster enters the small nanocluster size regime where over 50% of all atoms are in the cluster surface ($d < 3$ nm) the physical properties depend strongly on the surface chemistry and morphology. Additionally, quantum confinement of carriers plays an important role in determining the optical properties of metal and semiconductor nanoclusters. For example, 2 nm Au and Ag nanoclusters show extensive damping of the optical plasmon due to scattering at the interface with the embedding medium. We report experiments on a little studied nanocluster system, Sn. In the bulk Sn undergoes a structural phase transition from metallic white β -Sn with a distorted closed packed lattice to gray α -Sn, tetragonal, semi-metal diamond lattice at 180C. We investigate the nature of this transition as a function of cluster size using tools such as high resolution size exclusion chromatography (HRSEC) to explore the effect of size, shape, and chemical interface on the optical properties of Sn nanoclusters in dispersed solution. To study the size-dependent phase transformation in Sn nanoclusters, we use transmission electron microscopy (TEM) and selected area electron diffraction (SAD). We compare our observations to previous non-classical features in the optical absorbance of the smallest clusters of Au, Ag, and Cu which correspond to the development of discrete densities of states as the clusters approach molecular dimensions. The development of a small semiconductor gap in semi-metal like Sn has applications in areas such as sensors, NIR detectors, and robust scintillation phosphors. Acknowledgments: Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

SESSION R12: Synthesis of Nanoporous Materials II

Chair: Frank Endres
Friday Morning, April 1, 2005
Room 2009 (Moscone West)

10:00 AM *R12.1

Porous and Nanoporous Semiconductors and Emerging Applications. Helmut Foell, Juergen Carstensen and Stefan Frey; Chair for General Materials Science, Faculty of Engineering, Christian-Albrechts-University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany.

Electrochemical etching of semiconductors under certain

circumstances renders the materials porous. Pore diameters and distances between pores (= pore geometry) may vary from about 1 nm to $> 10 \mu\text{m}$; and in some cases the pore arrangement can be defined by lithography. Pore morphologies span the range from perfectly cylindrical pores, either in a crystallographic direction or in the direction of the electrical field driving the etching current, to sponge-like pores with all kinds of intermediate configurations. Many instances of self-organization have been observed; the most conspicuous one is the formation of single crystals of nanopores in InP. It is also possible to generate porous superstructures by changing the pore structure in a defined way during pore growth. However, not all combinations of geometry and morphology are possible in all semiconductors, and the possibilities and limits of pore formation in semiconductors are not fully understood at present and constitute an active research area. Porous semiconductors can be seen as meta-materials with properties that may be completely different from the properties of the bulk material, this is particularly valid for nanoporous materials. Not only the surface to volume ratio hugely is increased, offering wide possibilities to functionalize the surface and to influence the bulk behaviour via surface state induced carrier manipulation, but bulk properties like conductivity, luminescence, effective index of refraction, phonon spectra, or second harmonic generation, may not only be very different from the bulk properties of the semiconductor, but also from some linear average of the properties of the host and the (air-filled) pores. A case in point are optical properties; where the symmetry-breaking induced by crystallographic pores may induce birefringence or even more unusual anisotropies in the refractive index, or strong enhancements of second harmonic generation. If the pores are filled with other materials (e.g. metals or polymers) nanocompounds with unusual properties (e.g. strong plasmon resonances) may result. While many properties of porous semiconductors are not yet fully understood or even discovered, a wide range of possible applications has already emerged. More exotic ones use nanoporous Si as high-energy explosives for airbags, as nearly perfect antireflection layers for solar cells or as "Brownian motors"; self-organized nanopores in InP may serve as easy-to-make integrated wave-guides. More conventional applications of porous semiconductors include sensors for gases or biological molecules, photonic crystals, electrodes for micro fuel cells, bio-"chips", MEMS structures, or nanotemplates for nanorods or nanotubes. Moreover, functionalized or "natural" surfaces may exhibit "switchability" - membranes made from porous Ge, e.g., can be switched via the external potential from hydrophobic to hydrophilic behavior and thus may find use in advanced filtering technologies.

10:30 AM R12.2

Nanoporous Ceramic and Composite Membranes from Anodic Alumina. Dmitri Routkevitch, Oleg Polyakov and John Valdez; Synkera Technologies Inc., Longmont, Colorado.

This presentation will overview Synkera's recent efforts in the development of innovative ceramic and composite membranes and membrane reactors based on self-organized nanoporous anodic aluminum oxide (AAO). The focus of this talk will be on hydrogen generation and separation applications in support of anticipated demand for distributed and point-of-use hydrogen production and purification (e. g. portable fuel cells). Blank AAO membranes used in this efforts have intrinsically defect-free symmetrical morphology with high density cylindrical pores that are aligned perpendicular to the membrane plane, pores size in the 1-100 nm range with pore size distribution (STD better than 10%), high pore density (1×10^2 to 1×10^8 cm⁻²), size up to 90 nm, and thickness up to 0.2 mm thickness. Membranes from polycrystalline gamma- and alpha-alumina retain overall integrity and nanoporous morphology, and could be used up to 800C and 1000C respectively. Presented ceramic membrane-reactors for hydrogen generation are fabricated via conformal deposition of catalytic materials onto the pore walls of AAO, with membrane performance rooted in the nanoscale engineering of membrane architecture and composition. Composite hydrogen separation membranes are enabled by an advanced architecture integrating an ultra-thin Pd-based active layer, which could potentially support significant increase in hydrogen flux with no reduction in hydrogen selectivity.

10:45 AM R12.3

Curved Mesoporous Silica by Nano-confinement. Yiying Wu¹, Kirill Katsov², Scott W. Sides³, Glenn H. Fredrickson^{3,4}, Martin Moskovits¹ and Galen D. Stucky^{1,4}; ¹Chemistry, UC Santa Barbara, Santa Barbara, California; ²Materials Research Lab, UC Santa Barbara, Santa Barbara, California; ³Chemical Engineering, UC Santa Barbara, Santa Barbara, California; ⁴Materials, UC Santa Barbara, Santa Barbara, California.

In a physically confined environment, interfacial interactions, symmetry breaking, structural frustration, and confinement-induced entropy loss can play dominant roles in determining molecular organization. Here we present a systematic study of the confined

assembly of silica-surfactant composite mesostructures within cylindrical nanochannels of varying diameters. Using exactly the same precursors and reaction conditions that form the 2-dimensional hexagonal SBA-15 mesostructured thin film, unprecedented silica mesostructures with chiral mesopores such as single- and double-helical geometries spontaneously form inside individual alumina nanochannels. By tightening the degree of confinement, a transition is observed in the mesopore morphology from a coiled cylindrical to a spherical cage-like geometry. Self-consistent field calculations carried out to account for the observed mesostructures accord well with experiment. The mesostructures produced by confined syntheses are useful as templates for fabricating highly ordered mesostructured nanowires and nanowire arrays, and also as membranes for size-selective and potentially enantio-selective molecule separations.

11:00 AM R12.4

Generation of Functional Mesoporous Thin Films of Binary Metal Oxides with Crystalline Pore Walls using Novel Block Copolymer Templates and Characterization by Suitable Analytical Techniques. Bernd Smarsly¹, Torsten Brezesinski¹,

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Mesoporous metal oxide thin films have attracted significant attention due to their potential use in photocatalysis, redox reactions, electrochromic devices, sensing etc. A straightforward method for there is sol-gel chemistry in combination with a suitable structure-directing amphiphilic block copolymer. Typically, a substrate is dip-coated by a solution containing a metal salt (chlorides, alkoxides) as precursor in the presence of a template, leading to the formation of the corresponding mesoporous oxide after temperature treatment. However, the fabrication of such films with entirely crystalline walls (e.g. titania, ceria) was reported to show severe difficulties due to mesostructural collapse. Several other metal oxides have not been reported at all in the form of crystalline mesoporous thin films. In the present study, a general methodology is introduced for the generation of thin mesoporous films of various oxides, for the first time crystalline mesoporous MoO₃, WO₃ and tantalum oxide films were obtained. Our approach is based on the use of a novel block copolymer template in combination with suitable dip-coating and temperature treatment conditions. The polymer (KLE) was synthesized in our institute and has a hydrophilic PEO block and a poly(ethylene-co-butylene) hydrophobic block, thereby possessing advanced templating properties in terms of the thermal stability and hydrophilic-hydrophobic contrast [1,2]. Also, the block lengths were designed to be long enough to allow for sufficiently thick walls, i.e. nanocrystals in the pore walls of at least 5 nm, being compatible with the nucleation of oxide particles inside the walls without destroying the mesostructure. It is demonstrated that the superior templating properties of this block copolymer enables the development of facile procedures to obtain crystalline thin films of various oxides, especially tungsten oxide, hafnia, molybdenum oxide, tantalum oxide and ceria. The crystallisation and mesostructural changes upon temperature treatment were studied by In-situ Small-angle and Wide-Angle x-ray scattering (SAXS/WAXS) using the synchrotron facility at Elettra (Italy). These studies revealed that KLE allows a much better compatibility of the crystallization with the mesostructure than standard templates like Pluronic. Furthermore, the mesostructure and crystallinity was carefully studied by a new evaluation approach for the SAXS of such films, in combination with Electron Microscopy, and nitrogen, krypton and water sorption. Together with Atomic Force Microscopy, by our SAXS analysis the size and aspect ratio of the deformed spherical pores could be determined in thin films with Angstrom precision for the first time. Owing to their crystalline nature, these metal oxides films show the typical functionality, e.g. electrochromic behavior for tungsten oxide and molybdenum oxide. [1] Thomas et al. Langmuir 2003, 19, 4455. [2] Smarsly et al. Chem. Mater. 2004, 16, 2948.

11:15 AM R12.5

Synthesis Conditions of Ordered Mesostructured Boron Nitride Prepared from Borazinic Precursors and CMK-3 Carbon Template. P. Dibandjo, L. Bois, F. Chassagneux and P.

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Hexagonal boron nitride (BN) has some interesting chemical, thermal and electrical properties.^[1] Porous boron nitride could be very useful as holding catalysts, sensors, chromatography or purification materials, since it could be used in air at high temperature.^[1-3] New synthesis ways of porous boron nitride should be found, as for

instance those involving mesoporous material nanocasting process.^[4] The hard-template route seems to be convenient to prepare mesostructured non-oxide ceramics, since impregnation of a template can be performed using a liquid ceramic precursor, followed with a ceramization step. Mesoporous silica nanocasting has been used to synthesize mesoporous carbon CMK.^[5-6] There is already some promising studies dealing with non-oxide periodic nano-structured ceramics.^[7-8] Here, we describe borazinic precursor infiltration in mesoporous carbon using liquid phase infiltration technique. A ceramization step is used to transform the borazinic precursor into boron nitride. The carbon template is then removed by a thermal treatment. Two borazines have been used : The tri(methylamino)borazine (HNB(NHCH₃)₃) (MAB), already used for the preparation of boron nitride fibers^[9-10] and the trichloroborazine (HNBCl)₃, (TCB). The CMK-3 hexagonal mesoporous carbon has been used, which allowed the SBA-15 replication.^[11-12] The BN mesoporous materials obtained have been studied by X-ray diffraction, FTIR spectroscopy, TEM, SEM and pore size analysis. Different parameters of the synthesis of porous boron nitride materials are discussed: the nature of borazinic precursor, the infiltration process, the ceramization step and the technique used for the carbon template elimination. Ordered mesoporous boron nitride can be obtained with 4 nm diameter pores, 0.4 cm³/g mesoporous volume and high specific surface area (800 m²/g). **References** [1] R.T. Paine, C.J. Narula, Chem. Rev. 1990, 90, 73. [2] D.A. Lindquist, D.A. Smith, A.K. Datye, Mat. Res. Soc. Symp. Proc. 1990, 180, 73. [3] J.A. Perdigon-Melon, A. Auroux, B. Bonnetot, J. Solid State Chem. 2004, 177, 609. [4] J.S. Beck, J.C. Vartuli, M.E. Leonowicz, C.T. Kresge, J. Am. Chem. Soc. 1992, 114, 10834. [5] R.Ryoo, S.H. Joo, S.Jun, J. Phys. Chem. 1999, 103, 7743. [6] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M., Jaroniec, J. Am. Chem. Soc., 2000, 122, 10712. [7] H. Wang, X.D.Li, J.S.Yu, J. Mater. Chem. 2004, 14, 1383. [8] P. Krawiec, C. Weidenthaler, S. Kaskel, Chem.Mater. 2004, 16, 2869. [9] S. Bernard, D. Cornu, P. Miele, H. Vincent, J. Bouix, J. Organomet. Chem. 2002, 657, 91. [10] Y. Kimura, Y. Kubo, N. Hayashi, Composites Sci. & Tech. 1994, 51, 173. [11] M. Kang, S.H. Yi, H.I. Lee, J.E. Yie, J.M. Kim, Chem. Comm. 2002, 1944. [12] A. H. Lu, W. Schmidt, A. Taguchi, F. Schuth, Angew. Chem. Int. Ed. 2002, 41, 3489.

11:30 AM R12.6

Atomic Layer Deposition for the Conformal Coating of Nanoporous Materials. Jeffrey W. Elam¹, Guang Xiong²,

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Atomic layer deposition (ALD) utilizes a binary reaction sequence of self-saturating chemical reactions between gaseous precursor molecules and a solid surface to deposit films in a monolayer-by-monolayer fashion. These attributes make ALD an ideal method for applying very precise, conformal coatings over nanoporous materials. In this presentation, we describe recent work exploring the ALD coating of two nanoporous solids: anodic aluminum oxide (AAO) and silica aerogels. The AAO and silica aerogels have been successfully coated by ALD with a variety of oxide films including Al₂O₃, ZnO, TiO₂, and V₂O₅ as well as some metal films. These materials were characterized with a host of analytical techniques including SEM, TEM, EDX, AFM, XRD and BET surface area measurements. The ALD coated AAO materials are being employed as mesoporous catalytic membranes, size-specific separations membranes and sensors. For instance, to fabricate the catalytic membranes from the AAO templates, the pore diameter of the AAO membranes is first reduced to the 5-10 nm regime using Al₂O₃ ALD. Next, TiO₂ ALD is used to deposit several monolayers of catalytic support material. Finally, the active V₂O₅ catalyst is deposited by ALD. The resulting nanostructured catalytic membranes show remarkable selectivity in the oxidative dehydrogenation of cyclohexane when compared to conventional powder catalysts. In addition to the AAO membranes, silica aerogels have been coated using ALD. Silica aerogels have the lowest density and highest surface area of any solid material. Consequently, these materials serve as an excellent substrate for fabricating catalytic materials by ALD. In addition to their use as catalysts, the ALD modified aerogel materials have applications in hydrogen storage and production, and chemical sensing. In this study, both thin film and monolithic aerogels were coated by ALD and the coating process was investigated as a function of the reactant exposures.

11:45 AM R12.7

Growth Characteristics of Self-Assembled Mesoporous Nanospheres of Platinum and Platinum-Ruthenium.

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Use of nanostructured materials has proven to be a highly effective method of increasing apparent reaction rates by dramatically increasing surface area where local rates are only modest. This concept is important in catalysis and is of particular significance for noble metal applications. Direct methanol fuel cells (DMFCs) are one example of such use. The DMFC commonly uses both a platinum cathode catalyst and a mixed metal of platinum and ruthenium anode catalyst. The present work will report a method to grow spontaneously self-assembled mesoporous nanospheres of either platinum only or a platinum-ruthenium co-deposit, which are evenly distributed in all three spatial directions within a conductive carbon matrix. Surface area analysis by hydrogen adsorption/desorption for the platinum deposits reveals that the nanospheres are mesoporous. SEM shows that nanospheres of platinum-ruthenium have a morphology similar to platinum. Additionally, results of varying deposition conditions to optimize methanol oxidation and the effect on catalyst morphology will be discussed for the platinum-ruthenium samples. Potentiostatic electrodeposition of platinum ions from an aqueous salt solution, or a co-reduction from a mixture of platinum and ruthenium ions, was carried out on a carbon matrix and monitored coulometrically for loading. SEM micrographs were taken at various loadings. Both platinum and platinum-ruthenium spheres have a similar size and shape with platinum being just under 200nm in diameter and platinum-ruthenium being just over. Additionally, the spheres do not change appreciably in size from low loadings to high loadings. The spheres appear to grow rapidly to approximately 180nm and slow nearly completely, while new spheres nucleate and grow rapidly. This process continues through the deposition such that only the number density of the spheres in the carbon matrix increases with further loading, not the size of the spheres. High-resolution SEM and surface area analysis reveal porosity in the spheres, while the extent of accessible pore area for methanol oxidation is under study. Deposition conditions such as applied potential and metal ion concentrations in the precursor solutions show a strong effect on final catalyst activity toward methanol oxidation, and to a lesser extent, the catalyst morphology. Both lower concentration precursor solutions and more negative deposition potentials give a marked increase in methanol oxidation activity. In either case, these conditions suggest that deposition near a diffusion limited current condition gives a stronger performing catalyst. SEM characterization and quantitative mass analysis will be presented, illustrating the relationship of morphological changes on increased oxidation activity.