Monday Afternoon, November 4, 2002

Nanotubes: Science and Applications Topical Conference
Room: C-209 - Session NT-MoA

Nanotubes: Chemical Functionalization, Sensors
Moderator: V.I. Merkulov, Oak Ridge National Laboratory

2:00pm NT-MoA1 Photoenhanced Oxygen Adsorption in Carbon Nanotubes, *A.M. Rao*, Clemson Univeristy   **INVITED**
Thermopower (TEP) measurements have been very effective for detecting trace amounts of absorbed gases in single walled carbon nanotube bundles (SWNTs). The dynamics of gas adsorption is extremely rapid with a short time constant (few seconds to hours) for achieving oxygen saturated TEP values of ~ +45 µV/K in SWNT bundles. Upon desorbing the oxygen from the sample, the TEP switches reversibly to ~ -45 µV/K. In this talk, we present TEP values in films of multiwalled carbon nanotubes (MWNTs) as a function of exposure to room air in the presence or absence of illumination from a UV lamp. The MWNT films were prepared on quartz substrates from a thermal decomposition of xylene-ferrocene mixtures at ~700 °C. In room air and room light, freshly prepared MWNT films exhibit a negative TEP value of ~ -12 µV/K that systematically changes to ~ +12 µV/K over a time period of ~ 4 months. Thus, MWNTs offer a unique opportunity to study photoinduced adsorption of gases in quasi one dimensional carbon system. Interestingly, upon UV illumination of the MWNT film in room air, the rate at which TEP sign reverses is drastically reduced to 7-10 days suggesting a photoenhanced oxidation phenomenon in carbon nanotubes. Based on our density functional calculations, we attribute this photoinduced phenomenon due to the lower energy barrier for adsorption of photogenerated singlet oxygen in the MWNT films. This work was done in collaboration with T. Savage, S. Bhattacharya, B. Sadanadan, J. Gaillard, T. M. Tritt, and Ya-Ping Sun (Clemson University), and S. Nayak (Rensselaer Polytechnic Institute). Research was supported by a grant from NASA Ames Research Center.

2:40pm NT-MoA3 Strategies for Carbon Nanotube Functionalization, *S. Wong*, S. Banerjee, SUNY at Stony Brook
Understanding the chemistry of single-walled carbon nanotubes (SWNTs) is critical to rational manipulation of their properties. In one set of experiments, raw and oxidized SWNTs have been reacted with metal-containing molecular complexes. One of the molecular complexes studied was Vaska's compound. It has been found that Ir coordinates to these nanotubes by two distinctive pathways. With raw nanotubes, the metal attaches as if the tubes behaved as electron-deficient alkenes. With oxidized nanotubes, the reaction occurs by coordination through the increased number of oxygen atoms, forming a hexacoordinate structure around the Ir atom. Another compound analyzed was Wilkinson's complex. It has been found that the Rh metal similarly coordinates to these nanotubes through the increased number of oxygenated species. The functionalization reaction, in general, appears to significantly increase oxidized nanotube solubility in DMF (in the case of Vaska's) and in DMSO (with Wilkinson's). The derivatization process results in exfoliation of larger bundles of SWNTs and may select for the presence of distributions of smaller diameter tubes. An application has been made of this system as supports for homogeneous catalysis. In another set of experiments, oxidized SWNTs have been reacted with cadmium selenide nanocrystals (quantum dots) as well as with titanium dioxide nanocrystals to form nanoscale heterostructures, characterized by transmission electron microscopy and infrared spectroscopy. Based on the types of intermediary linking agents used, we have demonstrated a level of control over the spatial distribution of nanocrystals on these tubes. Optical data on the derivatized adducts suggest the possibility of interesting charge transfer behavior across the nanocrystal-nanotube interface.

3:00pm NT-MoA4 The Fabrication and Characterization of Carbon Nanotube Nanoelectrode Array for Chemical/Biosensor Applications, *J. Li*, R. Stevens, NASA Ames Research Center / Eloret Corp., H.T. Ng, NASA Ames Research Center / SETI Institute, L. Delzeit, NASA Ames Research Center, A. Cassell, C. Nguyen, B. Chen, J. Han, NASA Ames Research Center / Eloret Corp., M. Meyyappan, NASA Ames Research Center
Nanoelectrode arrays are attractive electroanalytical tools with the potential to provide much higher sensitivity for chemical and biosensor applications. So far nanoelectrode arrays/ensembles were prepared by template synthesis using nanoporous membranes or nanoscale defects created in the self-assembled organic monolayers on an Au surface. We report here on a new approach to fabricate solid-state nanoelectrode array/ensemble by bottom-

up scheme using well-aligned multi-walled carbon nanotube arrays on a conducting substrate. Carbon nanotubes were grown on a substrate prepatterned with metal catalysts. The density can be controlled precisely with e-beam lithography. The alignment, diameter, and length can be controlled by plasma CVD process. Dielectric material such as SiO2 was then filled into the gap between carbon nanotubes by TEOS CVD to insulate the sidewall of the carbon nanotubes as well as the conductive underlayers. This method also provides an added advantage by which the mechanical strength of the carbon nanotube array is dramatically improved. An aggressive mechanical polishing can thus be applied to planarize the surface, resulting in a flat surface with only the ends of carbon nanotubes exposed. SEM indicates that carbon nanotubes remain their integrity during these processes. AFM shows that carbon nanotubes extend out of the insulating matrix by a few nanometers due to the higher mechanical strength. The electrical properties of individual carbon nanotubes in the array are thoroughly characterized with current sensing AFM and I-V measurements. Both of metallic and semiconducting properties were observed, strongly depending on the growth conditions. Thus fabricated carbon nanotube array is essentially an ideal nanoelectrode array with graphite edge-plane like nanoelectrodes distributed in a controlled way. The electrochemical properties and the application of these nanoelectrode arrays as chemical and biosensors will be discussed.

3:20pm NT-MoA5 Investigation on the NO2 Sensitivity Properties of Multi-Wall Carbon Nanotubes Prepared by Plasma Enhanced Chemical Vapor Deposition, *C. Cantalini*, University of L'Aquila, Italy, L. Valentini, I. Armentano, J.M. Kenny, University of Perugia, Italy, L. Lozzi, S. Santucci, University of L'Aquila, Italy
The special geometry and unique properties of carbon nanotubes offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors.[1-4] The effect of gas environment on the electronic properties of carbon nanotubes have recently attracted certain attentions.[5,6] In the present work multi-wall carbon nanotubes (MWNTs) deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO2. The sensor design is a MWNT serpentine resistor, fabricated by photolithography defining a serpentine Si3N4 path upon silicon, and then growing MWNTs upon the Si3N4 structure. The electrical response has been measured exposing the films to NO2 (5 ppm) at different operating temperatures ranging between 50 and 250 Â°C. Upon exposure to NO2 the electrical resistance of MWNTs is found to decrease. The nanotube sensors exhibit a fast response and a substantially higher sensitivity than that of existing solid-state sensors at room temperature. Sensor reversibility is achieved by slow recovery under ambient conditions or by a higher recovery heating to 200 Â°C. Experimental findings revealed the chemisorption of oxidizer gas upon the surface of the NWNTs. Hence it appears that p-type semiconductor behavior is present in the MWNTs.

[1]Dresselhaus M S et al. 1996 Scienceof Fullenrenes and Carbon Nanotubes (New York:Academic)
[2]Ebbesen T (ed) 1997 Carbon Nanotube: Preparation andProperties (Boca Raton, FL: CRC Press)
[3]Saito R et al. 1998 PhysicsProperties of Carbon Nanotubes (New York: WorldScientific)
[4]Lu J P et al. 1998 Int. J. High Electron. Syst. 9 101
[5]Kong J et al. 2000 Science 287 622
[6]Collins P G et al. 2000 Science 287 1801 .

3:40pm NT-MoA6 Invited Paper, *R. Baughman*, University of Texas at Dallas   **INVITED**

4:20pm NT-MoA8 Surface Modification of Aligned Carbon Nanotube Arrays, *L. Dai*, The University of Akron
The excellent optoelectronic, mechanical, and thermal properties of carbon nanotubes have made them very attractive for a wide range of potential applications. However, many applications require the growth of aligned/micropatterned carbon nanotubes, along with their surface modification. We have developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate surface. We have also used photolithographic and soft-lithographic techniques for patterning the aligned carbon nanotubes with a sub-micrometer resolution. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest (e.g. polymer films for organic optoelectronic devices) in either a patterned or non-patterned fashion. The well-aligned structure further allows us not only to prepare novel aligned conducting polymer-carbon nanotube coaxial nanowires by electrochemically depositing a concentric layer of an appropriate conducting polymer onto the individual aligned carbon nanotubes, but also to develop a facile approach for modification of carbon nanotube surfaces via plasma activation followed by chemical reactions characteristic of the plasma-induced functionalities. These surface modification methods are

particularly attractive, which allow surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be retained. In this talk, results from our recent work on microfabrication and chemical modification of aligned carbon nanotubes for certain device applications (e.g. biosensors) will be presented.

4:40pm **NT-MoA9 Comparing Light Gas Diffusion Rates in Carbon Nanotubes and Zeolites**, *A.I. Skoulidas*, Carnegie Mellon University, *D. Ackerman, J.K. Johnson,* University of Pittsburgh, *D.S. Sholl,* Carnegie Mellon University

As in all microporous materials, the diffusion rates of molecules adsorbed in carbon nanotubes may have a large impact on the feasible applications of these materials. We have used atomistic simulations to compare the diffusion rates of H_2 and CH_4 in a range of defect-free single-walled carbon nanotubes with two silica zeolites with similar pore sizes, silicalite and ZSM-12. One advantage of comparing our results with these two zeolites is that we can validate the accuracy of our simulations against a large body of experimental data. We have used equlilibrium Molecular Dynamics and Monte Carlo methods to determine both the self diffusivity and the transport diffusivity of H2 and CH4 adsorbed as single components in carbon nanotubes. The transport diffusivity is the relevant quantity for describing macroscopic mass transfer in applications such as reversible adsorption cycles and membranes. We find that diffusion in carbon nanotubes is orders of magnitude faster than in the two zeolites over a broad range of pressure and temperature. These diffusivities are in fact among the fastest known for light gases in any environment, including bulk gas phases. This dramatic result can be understood in terms of the smoothness of the potential energy surface created by carbon nanotubes. We will discuss the implications of our results for using carbon nanotubes for highly permeable membranes.

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