

Applied Surface Science Room 324/325 - Session AS-MoA

Nanotube and Nanoparticle Characterization

Moderator: M.C. Burrell, GE Global Research

2:00pm AS-MoA1 Vibrational Behavior of Adsorbed CO@sub 2@ on the Interior and Exterior Surfaces of Carbon Nanotubes: An Experimental and First Principles Study, W.-L. Yim, O. Byl, P. Kondratyuk, J.K. Johnson, J.T. Yates, Jr., University of Pittsburgh

We have used CO@sub 2@ as a probe for the adsorption sites on single-walled carbon nanotubes (SWNTs). CO@sub 2@(g) shows an intense infrared band at 2349 cm@super -1@, due to the asymmetric CO@sub 2@ stretching mode. When CO@sub 2@ is adsorbed on (10,10) nanotube surfaces, this mode should be red shifted to a lower vibrational frequency. We measured the infrared spectrum of CO@sub 2@ adsorbed on SWNTs and have observed absorption peaks at 2341 cm@super -1@ and 2329 cm@super -1@. After ozone treatment and annealing in vacuum to 823 K, CO@sub 2@ adsorption causes the mode at 2329 cm@super -1@ to increase dramatically in intensity, with the peak at 2341 cm@super -1@ less affected. We have performed density functional calculations using the local density approximation on (10,10) SWNTs, with CO@sub 2@ adsorbed on interior, exterior, groove, and interstitial sites of bundles of the nanotubes. The CO@sub 2@ in the groove site and in the nanotube interior exhibit vibrational red shifts of 20.9 cm@super -1@ and 23.2 cm@super -1@, respectively, for the asymmetric stretching mode. This agrees very well with the experimental results for the larger shift. The CO@sub 2@ on the nanotube exterior has a theoretical red shift of 14.8 cm@super -1@ from the gas phase CO@sub 2@ mode, which may contribute to the peak at 2341 cm@super -1@ in the experiments. We have monitored the replacement of CO@sub 2@ by Xe through a series of co-adsorption experiments. Xe selectively replaces the CO@sub 2@ species giving the mode at 2329 cm@super -1@ and assigned to CO@sub 2@ bound inside the nanotubes. Thus, both experiments and simulations indicate that the more red-shifted absorption peak is due to CO@sub 2@ adsorbed on the inside and possibly the groove sites of the SWNT bundles. This work was supported by the Army Research Office.

2:20pm AS-MoA2 Adsorption and Dimerization of NO Inside of Single Walled Carbon Nanotubes - An Infrared Spectroscopic Study, P. Kondratyuk, O. Byl, J.T. Yates, Jr., University of Pittsburgh

The physical adsorption of NO on purified (10,10) single walled carbon nanotubes was investigated at low temperatures by means of transmission infrared spectroscopy. Ozone treatment followed by annealing was used as a method of opening the entry ports for adsorption into the interior of the nanotubes. The IR spectra show that NO which is adsorbed inside of nanotubes exists exclusively in its dimer form, with no infrared bands of the monomer visible at a sensitivity level of 5 mole % NO. The internally adsorbed NO dimer species observed is cis-(NO)@sub 2@ with $\nu_{\text{sub 1@}}(\text{symmetric}) = 1853 \text{ cm@super -1@}$ and $\nu_{\text{sub 5@}}(\text{asymmetric}) = 1754 \text{ cm@super -1@}$. Introduction of Xe into the system leads to selective displacement of the internally-bound cis-(NO)@sub 2@ dimer. A large spectroscopic red shift of the symmetric [-0.80%] and the asymmetric [-1.96%] modes for cis-(NO)@sub 2@ adsorbed inside of nanotubes (relative to gas phase cis-(NO)@sub 2@) points to the strong interaction of the dimer with the nanotube interior. The enthalpy of dissociation of the adsorbed dimer molecule is $15.1 \pm 0.7 \text{ kJ/mol}$.

2:40pm AS-MoA3 Adsorption of CF@sub 4@ on Opened Single Walled Carbon Nanotubes, O. Byl, P. Kondratyuk, L. Chen, J.K. Johnson, J.T. Yates, Jr., University of Pittsburgh

Single walled carbon nanotubes are currently the subject of intensive studies because of their potential application as sorbents. This is due to the deep potential energy well for adsorption inside of the nanotube. To make accessible the interior of the nanotube O@sub 3@ was used as an oxidizer to attack the strained endcaps and also defect sites, causing local oxidation of carbon atoms there. The ozonolysis was followed by annealing in vacuum to decompose carbonyl functionalities formed during the ozone treatment. Infrared spectroscopy has been used to make the first experimental discrimination between molecules bound by physisorption on the exterior surface of carbon single walled nanotubes (SWNTs) and molecules bound in the interior. In addition, the selective displacement of the internally-bound molecules has been observed as a second adsorbate is added. SWNTs were opened by oxidative treatment with O@sub 3@ at

room temperature, followed by heating in vacuum to 873 K. It was found that at 133 K and 0.033 Torr, CF@sub 4@ adsorbs on closed SWNTs exhibiting its $\nu_{\text{sub 3@}}$ asymmetric stretching mode at 1267 cm@super -1@ (redshift = -15cm@super -1@). Adsorption on the nanotube exterior is accompanied by adsorption in the interior in the case of opened SWNTs. Internally-bound CF@sub 4@ exhibits its $\nu_{\text{sub 3@}}$ mode at 1247 cm@super -1@ (redshift = -35cm@super -1@). It was shown that at 133 K, Xe preferentially displaces internally-bound CF@sub 4@ species, and this counter-intuitive observation was confirmed by molecular simulations. The pseudo-one-dimensional confinement of CF@sub 4@ inside of (10,10) single walled carbon nanotubes does not result in the production of the splitting caused by transition dipole - transition dipole interaction which is observed in 3D ensembles of CF@sub 4@.

3:00pm AS-MoA4 Sidewall Chemistry of Carbon Nanotubes Investigated by STM, K.F. Kelly, Rice University

There is a great deal of interest in understanding and controlling the chemistry of carbon nanotube sidewall functionalization. Enhanced solubility, improved formation of composite materials, controlled modification of the electronic structure, and increased hydrogen storage capacity are a few of the applications that this technology may impact. In this talk we will present scanning tunneling microscope studies of partially and fully fluorinated single-walled carbon nanotubes. In addition, we have imaged carbon nanotube sidewalls modified by various solution chemistry methods. Differences in electronic structure and surface coverage produced by each method will be discussed.

3:20pm AS-MoA5 Iron-Oxide Nanoparticle Stability in an Ion Beam, K.H. Pecher, D.R. Baer, M.H. Engelhard, Pacific Northwest National Laboratory

The immense interest in nano-structured materials necessarily leads to application of various methods of surface analysis to examine the composition, chemical state and other properties of such materials. There are a variety of reasons why the chemical properties of nanoparticles may differ from bulk versions of similar material. We have been examining various types of iron metal and oxide nanoparticles to understand their chemical behavior. During the course of study 30 nm diameter iron oxide particles distributed on a silicon wafer or a gold coated wafer were exposed to 2 kV ions. In comparison to a 30 nm thick iron oxide film, the nanoparticles were significantly altered. Particles suspended on Au were significantly reduced while particles distributed on the uncoated wafer rapidly formed an iron silicide. Further studies show that aggregates of nanoparticles do not show the same reduction. The stability of nanostructures when subjected to various types of analysis may be a significant complication to the study of these interesting materials.

3:40pm AS-MoA6 Scanning Tunneling Spectroscopy of Boron Nitride Nanotubes; Evidence for a Giant Stark Effect, S. Aloni, University of California at Berkeley and Lawrence Berkeley National Laboratory; *M. Ishigami,* University of California at Berkeley; *A. Zettl,* University of California at Berkeley and Lawrence Berkeley National Laboratory

The Electronic properties of double-walled boron nitride nanotubes BNNT's were studied by scanning tunneling microscopy and spectroscopy at 7K. High resolution topographs of the tubes reveal information about the hexagonal boron nitride lattice as well as information about interlayer coupling between inner and outer tube. Tunneling spectra are also strongly dependent on the electronic coupling between the tube and the substrate. When the tube is well coupled to the substrate the spectra clearly show manifestation of a one dimensionality of the electronic structure and band gaps of 3.5eV. However, weakly coupled tubes display significantly higher apparent band gaps of 7-9.5 eV, indicating that the applied electric field is not fully applied across the tunneling gap between the STM tip and the tube. Simple analysis of the current-distance spectra shows that the actual BNNT bandgap is significantly smaller (3-5 eV) and is attributed to a second tunneling junction present between the tube and the under-laying substrate. Unlike their carbon analogues, BNNT are expected to be semiconducting with a chirality independent band gap of 5-5.5eV. We explain the low measured band gap values by a tip induced giant Stark effect, where the band gap is narrowed due to the high electric field as predicted in recent theoretical calculations by S.Louie et al.

4:00pm AS-MoA7 Size Dependency of Structural, Optical, and Photocatalytic Properties of TiO@sub 2@ Nanoparticles, W. Li, S.I. Shah, S. Lin, C. Ni, C.-P. Huang, University of Delaware

Polycrystalline TiO₂ anatase nanoparticles with different average sizes (12, 17, 23 nm) were synthesized by metallorganic chemical vapor deposition (MOCVD). The particle sizes were determined by x-ray diffraction and

Monday Afternoon, November 3, 2003

transmission electron microscopy. The specific surface areas varied between 50 and 150 m²/gm, as measured by Brunauer-Emmett-Teller (BET) method. The size effects on the thermodynamic stability of TiO₂ was analyzed by annealing samples in the temperature range of 700 to 800 oC. Only anatase to rutile phase transformation occurred. The transformation rate was accelerated with the decrease of initial particle size. The activation energy was calculated from the XRD data. The activation energy decreased from 298.85 to 180.28 kJ/mol as the initial anatase particle size decreased from 23 to 12 nm. Photoabsorption measurements showed a red shift of the absorption edges with the decrease in the particle size down to 17 nm. Below this particle size, a blue shift was observed. Photodegradation of 2-chlorophenol solutions under ultraviolet irradiation showed 17 nm sample had the highest photoreactivity. This result will be discussed on the basis of size related difference of light absorption efficiency, active surface area, and lifetime of charge carriers.

4:20pm **AS-MoA8 Determination of the Fermi Level of Isolated Single-Walled Carbon Nanotubes in Solution**, *K. Murakoshi*, Hokkaido University, Japan

Single-walled carbon nanotubes (SWNT) should be among the best candidates for ultra-small functional units in ultra-sensitive, low-energy consumption nano-devices. Several characteristics of the electronic band structure of individual SWNT have been obtained successfully employing recently developed experimental techniques in confocal micro Raman spectroscopy, scanning tunneling microscopy and fluorescence methodology. In addition to band profiles, information regarding absolute potential of energy levels of the states is known to be essential to nano-device fabrication. Several estimations of energy levels from measurements of work function were attempted in vacuums and in electrolyte solution; however, all of these measurements utilized bulk bundle SWNT, which display certain distributions with respect to size. The diameter-dependent absolute potential of individual tubes has never been observed experimentally. The present report reveals that the energy position of the Fermi level of individual SWNT relative to the vacuum level depends on tube diameter based on measurements of resonance Raman intensity of individual SWNT under electrochemical potential control. Absolute potential of the Fermi level was found to be extremely sensitive to tube diameter. Structural dependence of metallic tubes is larger than that of semiconducting tubes. The values obtained can provide absolute potential maps of single SWNT at interface.

4:40pm **AS-MoA9 Band Modulation in Various Nanopeapods and Its Origin**, *J. Lee, H. Kim*, Seoul National University, Korea; *S.-J. Kahng*, Korea University, Korea; *J. Ihm*, Seoul National University, Korea; *H. Shinohara*, Nagoya University, Japan; *Y. Kuk*, Seoul National University, Korea

Recent studies show interesting electronic properties of carbon nanotubes with various metallofullerenes. We have performed scanning tunnelling microscopy and spectroscopy study on these peapods. Two surprising characters were found: 1) large magnitude of the bandgap modulation (as large as ~1eV in Gd@sub 2@C@sub 92@ peapods and ~0.3eV in GdC@sub 82@ peapods) and 2) multiple oscillation of the conduction band edge in the position dependent spectroscopy near a defect. Our theoretical simulation results partly describe the main features in the experimental data. The modulation of band is caused by derived states from states of nanotube and metallofullerene. The conduction band oscillation was explained by many body screening effect around a defect. The observation of multiple fringe patterns near a potential barrier was predicted in the STM theory of Luttinger liquid near a perfect reflecting boundary, which expected a set of infinitely extending hyperbolars in the dI/dV(X,V) spectra. In the case of metallofullerene peapod, however, the finite barrier potential can result in curvilinear subbands surrounding the scattering potential. The current results imply that the transport properties of peapods may be dominated by the extent and strength of the scattering potential associated with the electronic structure of the inserted metallofullerenes. The recent transport measurement also supports our observation and calculation. A more detailed understanding of the phenomenon may require a many-body electron screening theory with the pseudo-2D geometry and external potential.

@FootnoteText@ @footnote 1@ Jinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara, and Young Kuk, Nature 415, 1005 (2002). @footnote 2@ Sebastian Eggert, Phys. Rev. Lett. 84, 4413 (2000) @footnote 3@ P.-W. Chiu, G. Gu, G.-T. Kim, G. Philipp, S. Roth, S.F. Fang, and S. Yang, Appl. Phys. Lett. 79(23), 3845-3847 (2001).

Author Index

Bold page numbers indicate presenter

— A —

Aloni, S.: AS-MoA6, **1**

— B —

Baer, D.R.: AS-MoA5, **1**

Byl, O.: AS-MoA1, 1; AS-MoA2, 1; AS-MoA3, **1**

— C —

Chen, L.: AS-MoA3, 1

— E —

Engelhard, M.H.: AS-MoA5, **1**

— H —

Huang, C.-P.: AS-MoA7, 1

— I —

Ihm, J.: AS-MoA9, 2

Ishigami, M.: AS-MoA6, 1

— J —

Johnson, J.K.: AS-MoA1, 1; AS-MoA3, 1

— K —

Kahng, S.-J.: AS-MoA9, 2

Kelly, K.F.: AS-MoA4, **1**

Kim, H.: AS-MoA9, 2

Kondratyuk, P.: AS-MoA1, 1; AS-MoA2, **1**;
AS-MoA3, 1

Kuk, Y.: AS-MoA9, 2

— L —

Lee, J.: AS-MoA9, **2**

Li, W.: AS-MoA7, **1**

Lin, S.: AS-MoA7, 1

— M —

Murakoshi, K.: AS-MoA8, **2**

— N —

Ni, C.: AS-MoA7, 1

— P —

Pecher, K.H.: AS-MoA5, 1

— S —

Shah, S.I.: AS-MoA7, 1

Shinohara, H.: AS-MoA9, 2

— Y —

Yates, Jr., J.T.: AS-MoA1, 1; AS-MoA2, 1; AS-MoA3, 1

Yim, W.-L.: AS-MoA1, **1**

— Z —

Zettl, A.: AS-MoA6, 1