

II.1.4 Nanoengineering of Hybrid Carbon Nanotube-Metal Nanocluster Composite Materials for Hydrogen Storage

Investigators

Kyeongjae (KJ) Cho, Assistant Professor of Mechanical Engineering; Bruce Clemens, Professor of Materials Science and Engineering; Hongjie Dai, Associate Professor of Chemistry; Anders Nilsson, Associate Professor of Stanford Synchrotron Radiation Laboratory; Deepak Srivastava, NASA Ames Nanotechnology Center, Zhenyu Zhang, Oak Ridge National Lab, External Collaborators; Seongun Park, Postdoctoral Researcher, Byeongchan Lee, Jason Sese, Won Lee, David Mann, Anton Nikitin, Graduate Researchers

Introduction

The objective of this project is to develop optimized nanocomposite materials for high-density H₂ reversible storage applications. Specifically, carbon nanotube-catalyst nanoparticle composite materials with well-controlled nanotube size will be developed, that are optimized to satisfy the target fundamental characteristics for hydrogen storage. A systematic design and fabrication process will be followed that will permit not only controlled growth of carbon nanotubes but also incorporation of nanoparticles to decorate the nanotubes to catalyze H₂ adsorption and desorption processes.

Background

Nanomaterials have diverse tunable physical properties as a function of their size and shape due to strong quantum confinement effects and large surface/volume ratios. A single wall carbon nanotube (SWCNT) has the same structure as a roll of a single graphene sheet, and it has a nanometer-sized diameter ranging from 4 to over 100 Å. Due to their large surface areas with relatively small mass, SWCNTs have been considered as potential materials for high capacity hydrogen storage. Theoretically, they can store hydrogen up to 7.7 wt%, if every carbon atom in SWCNTs chemisorbs one hydrogen atom. In addition, the subsequent physisorption of hydrogen on the surfaces of hydrogenated SWCNTs can increase the capacity of hydrogen storage even further. In spite of the strong potential of SWCNTs, current experimental findings are not very promising mainly due to the lack of control in preparing SWCNTs as a hydrogen storage medium. It has recently been shown that the hydrogen-carbon nanotube interaction energy is a very sensitive function of the nanotube size, and a sample of a wide range of CNT sizes would have only a small fraction of the CNT surface suitable for hydrogen storage. There is currently much skepticism on carbon nanotube hydrogen storage due to early experimental mistakes, and therefore we are developing a rational basis for high capacity hydrogen storage materials through the systematic nano-materials approach we are taking in this project. The framework of nanomaterial design, fabrication and characterization that we are following to optimize catalyzed nanotubes for hydrogen storage is illustrated in Figure 1.



Figure 1: Flow diagram of the project.

Results

We have initiated a systematic search process in material parameter space (particle composition and size) for optimized nanocomposite materials with high-density hydrogen reversible storage properties. The results to date from applying the four main thrusts of this approach are discussed below.

Nanoparticle Design and CNT Growth Modeling

Using the hierarchical multi-scale modeling approach described in Figure 2, we have investigated a rational simulation method to design metal nanoparticles for catalytic CNT growth applications. Figure 3 shows how metal nanoparticles are designed from continuum shape optimization to atomic structure relaxation to quantum simulation of chemical reactivity.

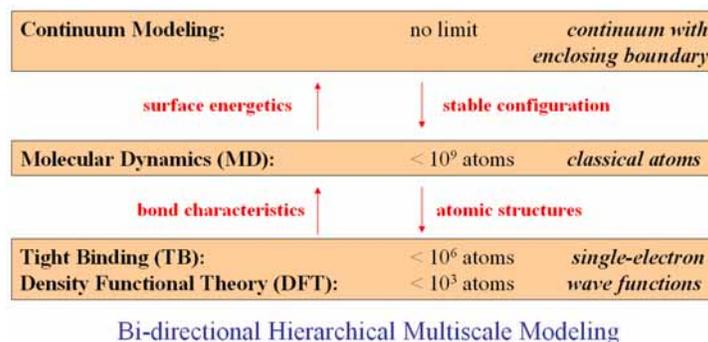


Figure 2: Framework for Multiscale Modeling of Nanoparticles

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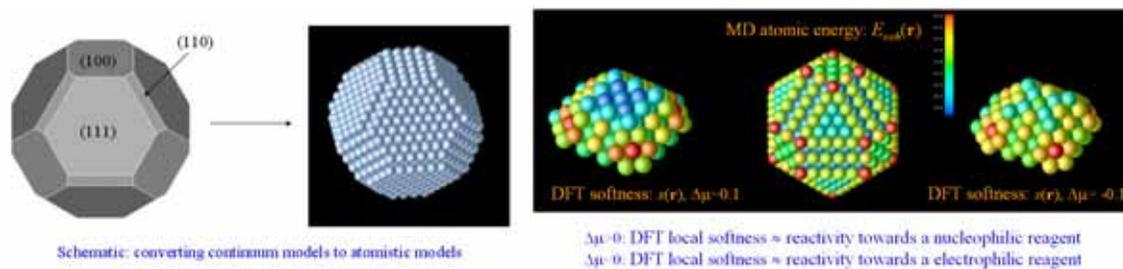


Figure 3: Sequence of Multiscale Modeling of a Pt Nanoparticle

To investigate the growth mechanisms of CNTs on metal nano-particle surfaces, we have investigated the hydrocarbon reaction on metal surfaces as illustrated in Figure 4 (left panel). Figure 4 (right panel) shows the results of CH_4 and C_2H_4 reactions on Ni(100), Ni(110) and Ni(111) surfaces. These results show that the reaction energies are $\Delta E = -1.193 \sim -1.411$ eV/C atom for CH_4 and $\Delta E = -2.221 \sim -2.439$ eV/C atom for C_2H_4 reactions, respectively. The difference in reaction energy indicates the efficiency of different hydrocarbons for CNT growth on Ni surfaces.

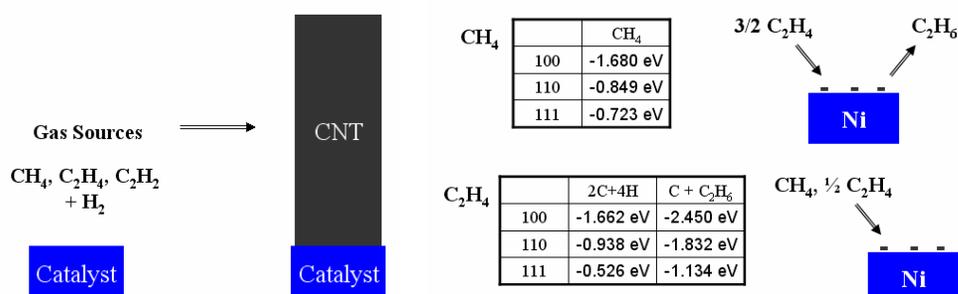


Figure 4: Modeling of CNT growth on metal surfaces

Metal Catalyzed Multi-Wall Carbon Nanotubes

It is clear from work at the National Renewable Energy Laboratory (NREL) and elsewhere that the content of nanostructured metal in carbon nanotube samples plays a critical role in the hydrogen storage capacity. For example, the storage capacity of nanotubes has been seen to greatly decrease after purification and removal of metal content. The form of the metal is also important, and the most effective form seems to be nanostructured metal particles in direct contact with the nanotube, such as the particles used in catalyzing nanotube growth. One interpretation of these results is that the metal is acting as a catalyst to assist in the hydrogen attachment process.

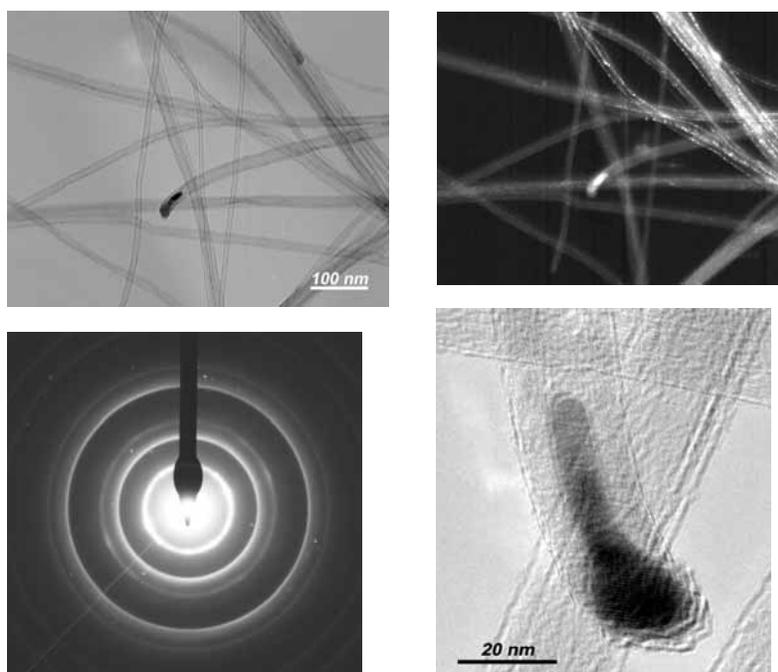


Figure 5: Transmission electron microscope results from an as-received multi-walled carbon nanotube sample. Upper left shows the bright field image, upper right shows the dark field image with the diffracting regions appearing bright. Lower left is the diffraction pattern, which shows rings from C-graphite and bcc Fe with about a 3% lattice expansion. The bright regions in the dark field picture are associated with both these phases. The bottom right shows a high-resolution picture of a Fe catalyst particle at the tip of a nanotube.

In order to investigate the effect of metals on the hydrogen storage process we are conducting a study of controlled introduction of metal to carbon nanotube structures. Our approach uses the flexibility and versatility of ultra-high vacuum sputter deposition to introduce controlled amounts of metal directly onto the surface environment, which have an average diameter of 15 nm and average wall thickness of 4.2 nm. Nanotubes of this type typically have a hydrogen storage capacity of around 1.5 wt.%. The metal in these nanotubes is in the form of catalyst particles formed in-situ during their growth from a Fe precursor. As shown in Figure 5, the metal catalyst nanoparticles remain at the end of the nanotubes. Our transmission electron microscopy (TEM) investigation and our magnetization results (Figure 6) show that the catalyst particles are bcc Fe on carbon nanotubes.

Figure 5 shows the results from our TEM study of a multi-walled carbon nanotube (MWCNT) sample obtained from NREL. These nanotubes were placed in an ultrahigh vacuum deposition chamber, and one monolayer of Fe was deposited by sputter deposition. Post-deposition transmission electron microscopy was inconclusive about the state of this deposited Fe. We are currently investigating (in collaboration with NREL

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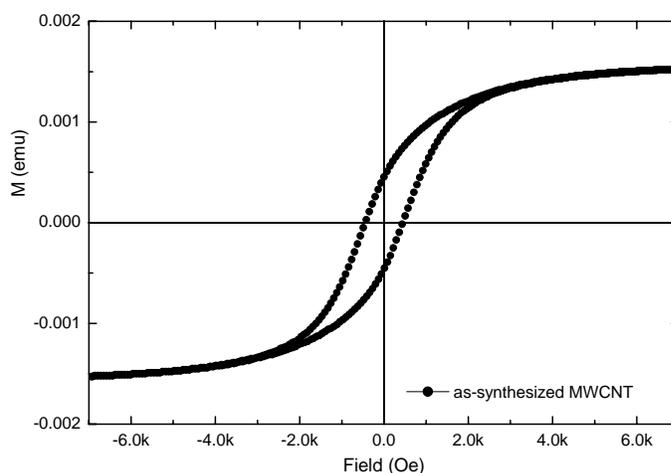


Figure 6: Magnetization results from an as-synthesized multi-walled carbon nanotube. Magnetization was measured in an ultra-sensitive alternating gradient magnetometer. The observed moment is from the Fe growth catalyst particles at the tip of the carbon nanotubes. The total mass of Fe for this sample was about 7 micrograms.

researchers) the change in hydrogen storage content associated with this controlled addition of metal. This initial investigation will be followed by a systematic study of the effects of the controlled addition of a variety of metals onto a variety of carbon nanostructures. We will work closely with the modelers on this team to design the ideal metal composition and morphology and investigate optimization of hydrogen storage capacity. These studies will be greatly assisted by availability of controlled structure nanotubes as our growth efforts progress, and will play a critical role in understanding and optimizing the hydrogen storage capacity of carbon nanostructures.

Single-Walled Carbon Nanotube Growth Control For Hydrogen Storage

One of the main ideas of our program is to control the size of SWCNTs to tune the H₂ storage capability. It is therefore critical to be able to synthesize bulk amounts of SWNTs with good structural control. To this end, we recently started a project to grow bulk quantities of SWCNTs using a Plasma Enhanced Chemical Vapor Deposition (PECVD) process we developed recently for growth on substrates. Growth is performed in a 4" remote PECVD system to produce high quality SWCNTs in bulk. Earlier experiments on SiO₂ substrates yielded tubes of fairly narrow diameter distribution that were nearly 90% semiconducting. To produce bulk catalyst, cobalt and iron acetate salts are dissolved in ethanol and loaded into a y-type zeolite support or fumed silica. These supports afford small, uniform catalyst particles, and can be removed using HF after growth.

Our latest growth result is a PECVD tube material with a narrow diameter distribution, centered around 1nm. Raman data taken at 514 nm and 785 nm reveal tubes with a similar diameter distribution to HipCo (high pressure Co, Smalley's process) and narrower than CoMoMAT (a material by the Resasco group known to have a narrow diameter distribution), and with evidence of a preponderance of semiconducting SWCNTs. From Figure 7, it appears that our PECVD SWCNTs exhibit a stronger Raman peak at around 260cm⁻¹ than the other materials, signaling that the nanotubes

mostly have diameters of around 1.2 nm.

We are currently optimizing the PECVD growth of SWCNTs by changing the catalyst support, metal compositions, loading percentages, temperature and plasma power. The growth parameter space will be fully explored to obtain SWCNTs with well-defined diameters.

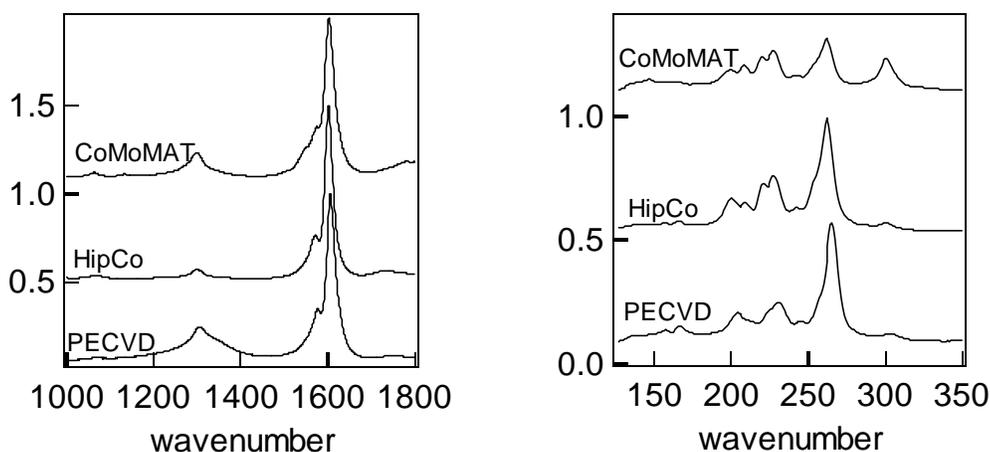


Figure 7: Raman Spectrum - 785nm Excitation of PECVD grown SWCNTs.

Spectroscopic Characterization of Hydrogen Storage

One of the key issues regarding hydrogen storage in carbon nanotubes is the mechanism for hydrogen adsorption. Hydrogen can adsorb in either a molecular form or as atomic hydrogen. In the molecular form, hydrogen can either physisorb on the walls of the nanotubes or condense inside the tubes. In the second form, where dissociation takes place, strong C-H bonds will be formed. In the current project we intend to design properties of the carbon nanotubes where the covalent bond energetics is optimized for an overall hydrogen storage performance. It is essential in the initial phase of this project to identify the mechanism of hydrogen storage and under which conditions we form C-H bonds.

We are in the process of performing the first synchrotron radiation studies of hydrogen adsorption to carbon nanotubes. Beam time is scheduled at the Advanced Light Source in Berkeley during the first two weeks in August 2004. It is important to first characterize the changes in x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) C1s spectra when atomic hydrogen is bonded to carbon atoms. The electronic structure of the substrate will undergo changes when the carbon atoms are rehybridized from sp^2 to sp^3 configurations. We are therefore currently building an atomic hydrogen source for dosing of hydrogen to the carbon nanotubes where we expect to obtain a reaction without the presence of a metallic catalyst for hydrogen dissociation. When we have a full understanding of the spectral changes due to C-H bond formation

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we will also dose molecular hydrogen to follow the reactions with the nanotubes in the presence of a catalyst.

In parallel, we are currently preparing for Infrared Reflection Absorption Spectroscopy (IRAS) measurements of hydrogen coordination to the nanotubes. We expect to observe both C-H stretch vibrations from covalent bonded H atoms and H-H vibrations from strongly physisorbed molecular hydrogen. The initial experiments will be carried out with the atomic hydrogen source and later with molecular hydrogen. The first experiments using IRAS will be carried out during the month of September. When we can identify H coordination we can perform temperature program desorption (TPD) measurements following the evolution of molecular hydrogen in the gas phase with a mass spectrometer and also through the change in the intensity of the C-H stretch vibrations. These measurements will provide information from which we can derive the strength of the C-H bond.

In order to perform *in situ* measurements, we are constructing a cell where atmospheric pressures of hydrogen can be applied to allow both IRAS and XAS measurements. The intention is to see if other channels of hydrogen coordination will appear when larger pressures are applied. We can use isotopic substitutions of H₂ and D₂ to follow the exchange reaction at different temperatures, which will bring insights in the energetics of hydrogen storage.

Progress

During the first five months of this project, we have started to move forward with the framework of nanomaterial design, fabrication and characterization to optimize catalyzed nanotubes for hydrogen storage. Nanomaterial design is proceeding with metal catalyst optimization as well as a simulation study of CNT growth processes on metal surfaces. For controlled growth of CNTs, we are making fast progress using PECVD to attain CNT size control. Using the existing MWCNT samples, nanoscale characterizations are moving forward as well as identifying specific hydrogen signatures for spectroscopic characterization of chemically and physically stored hydrogen in nanotubes.

Future Plans

Our research project team has successfully initiated the individual research components of nanomaterial design, nanoparticle and nanotube fabrications, and characterization as well as linking them into a rational material development framework. During the rest of 2004, we will move forward with full multi-scale design of nanoparticles with two graduate students, one post doctorate, and two collaborators (Dr. Srivastava and Dr. Zhang). Dr. Zhang will visit Stanford during the summer to join the nanomaterial design efforts. We would like to purchase a highly sophisticated nanoparticle generator and hydrogen measurement equipment to prepare the initial batch of optimized catalyst nanoparticles for controlled CNT growth. These CNTs will be used for atomic hydrogen adsorption to calibrate the hydrogen capacity of the nanotubes as well as for characterizing the nature of stored hydrogen in CNT samples.