IV.C.1k Controlling the Diameter of Single Walled Carbon Nanotubes for Hydrogen Storage

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Approach

Duke is developing methods to control the diameter of single walled carbon nanotubes (SWNTs) and the pore size of microporous carbon materials for tailoring the binding energy of hydrogen molecules on the surface of carbon-based materials. The overall goal is to design and synthesize materials with appropriate binding energies for hydrogen molecules that will show storage capacities meeting DOE 2010 goals in hydrogen storage properties. The diameter and pore size are predicted to be key parameters that can alter the binding energy with hydrogen [1,2]. Being able to systematically control such parameters will enable us to fabricate a series of materials with different binding energies for the study of its effect on storage capacity.

Duke is also developing methods that can systematically alter the binding energy of the materials through metal doping and boron doping in carbon-based materials, which are known to increase the binding energy of hydrogen on carbon [3,4]. Duke has developed methods to prepare microporous carbon materials using inorganic and/or organic templates that can control the pore sizes of the materials. Polymeric precursors were used to form the framework of the materials before conversion to carbon. New precursors with metal atoms and boron atoms can be used to introduce controlled doping of metal and boron. It will provide an additional handle that can alter the overall binding energy of hydrogen molecules over a larger range. Depending on the pore size and doping, the binding energy can be changed between a few kJ/mol to more than 20 kJ/mol, covering the predicted optimum binding enthalpy for hydrogen molecules in a temperature range between 77 K and room temperature.

FY 2007 Results

1. Developed understanding on the relation between the carbon feeding rate and the diameter of prepared nanotubes. Identified conditions under which small diameter carbon nanotubes (CNTs) can be prepared in bulk quantity. As shown in Table 1, the diameter of nanotubes prepared using powdered catalysts containing MgO, Mo and Co alter systematically as a function of the growth temperature:

TABLE 1. Relation between the Growth Temperature and the Composition of the Products

Growth Temperature	Products
750°C	SWNTs less than 1 nm in diameter
800°C	Mixture of SWNTs & double walled carbon nanotubes (DWNTs) with 1-1.5 nm average diameter
850°C	Mixture of DWNTs & SWNTs with more DWNTs, diameter around 1.5 nm
900°C	Mixture of DWNTs & triple walled carbon nanotubes (TWNTs), diameter between 2-3 nm
950°C	Mostly DWNTs and TWNTs, diameter between 2-3 nm.
1,000°C	Mostly CNTs with three and four walls, diameter around 4 nm.

   Small diameter SWNTs can be prepared by reducing the growth temperature to 750ºC. Such small diameter nanotube samples were provided to other Hydrogen Sorption Center of Excellence members for the characterization in comparison with other types of nanotubes. Samples were all measured at 77 K and 2 bar at the National Renewable Energy Laboratory (NREL). The results did not indicate a noticeable increase in the storage capacity. However, more measurements are needed to identify whether the binding energy of hydrogen molecules on such materials is different from nanotubes with larger diameters.

2. Prepared high purity DWNTs for testing of their hydrogen storage properties. A recent publication indicated that DWNTs exhibit better hydrogen

storage capacity than SWNTs [5]. To verify such claims, bulk quantity DWNTs were prepared at Duke (Figure 1) and provided to NREL for measurement. Initial test results did not indicate the improved storage capacity in the DWNTs.

3. Developed methods to prepare microporous carbon materials. Microporous carbon materials with controllable pore sizes were made using different surfactants as organic templates (Figure 2). The average pore size is around 1.3 nm for samples made using surfactant P123 as the template and 1.2 nm for samples prepared using surfactant P103 as the surfactant. Future focus of research is to shrink the pore size to less than 1 nm and to introduce dopants into the system.

FY 2008 Plans

1. Pore size control in microporous carbon materials.
   - Develop scalable method to synthesize microporous carbon materials using organic molecules as templates.
   - Use different surfactant molecules and different annealing temperatures to control pore size distribution of the materials. Compared with other approaches, such as carbide-derived carbon and zeolite-templated carbon materials, the approach will offer more flexible control of pore size and doping concentration. It also avoids the use of highly toxic chemicals like chlorine and hydrogen fluoride.

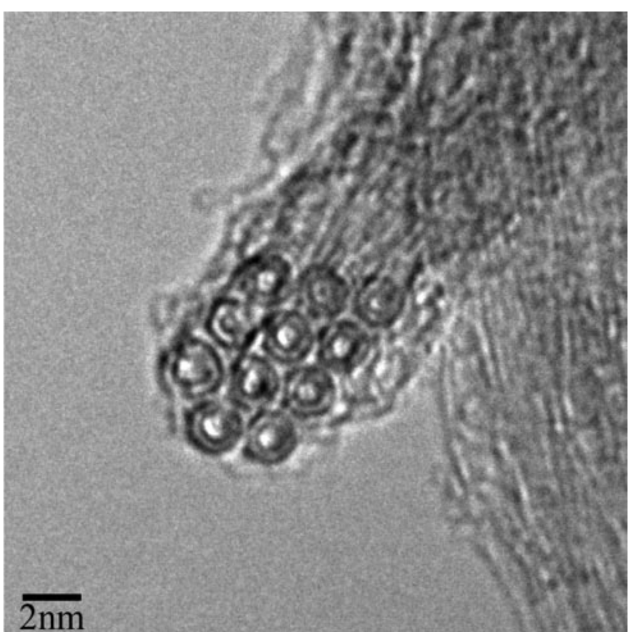

FIGURE 1. Transmission Electron Microscopy (TEM) Image of High Purity DWNTs

2. Doping of the porous carbon materials with metal atoms and boron atoms.
   - Develop methods to use precursors containing metal atoms and boron atoms to prepare microporous carbon with controlled doping.
   - Demonstrate the change of binding energy to hydrogen through doping.
   - Do systematic study on the effect of pore size and doping level to discover the optimum binding energy for hydrogen.
   - Demonstrate that the materials' storage capacity exceeds the DOE system goal of 6% by weight.

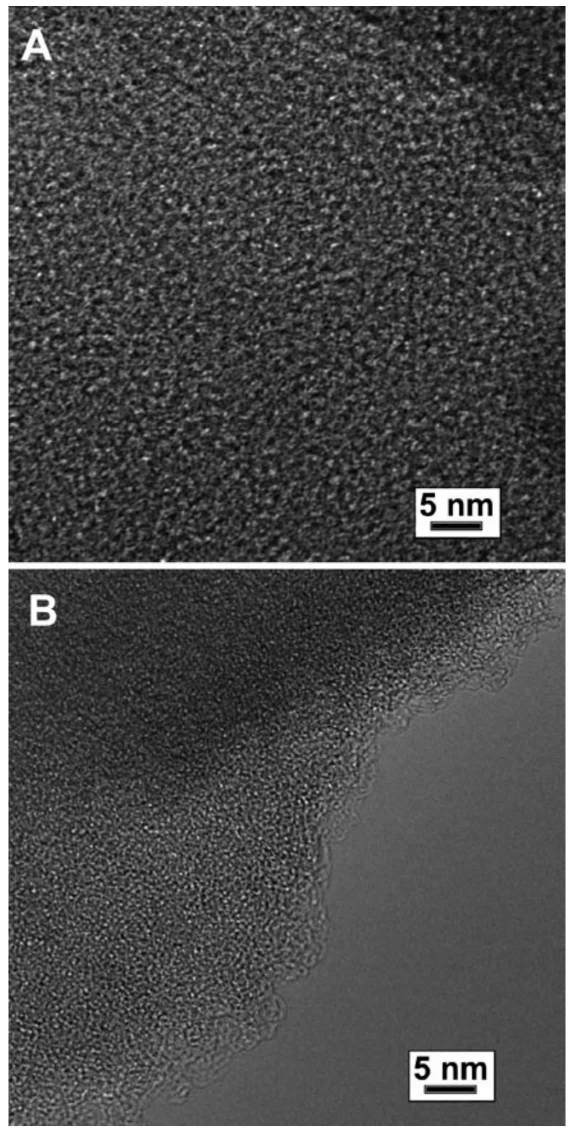

FIGURE 2. A) TEM image of microporous carbon materials prepared using P123 as the organic template. B) Samples made from using P103 as templates. The images showed the changes in the average pore size distribution as a function of different templates.

FY 2007 Publications/Presentations

Publications

1. "Synthesis of Double-walled Carbon Nanotubes Using Iron Disilicide as Catalyst", Hang Qi, Cheng Qian, Jie Liu, **Nano Letters,** Accepted (2007).

2. "Two-Stage Growth of Single-Walled Carbon Nanotubes". Hang Qi, Dongning Yuan, Jie Liu, **Journal of Physical Chemistry C,** 111(17); 6158-6160 (2007).

3. "Controlling the Diameter of Carbon Nanotubes in Chemical Vapor Deposition Method by Carbon Feeding", Chenguang Lu, Jie Liu, **Journal of Physical Chemistry B,** 110(41) 20254 - 20257 (2006).

Invited Presentations

1. "Understanding the Nucleation and the Growth of SWNTs in a CVD Process" Hang Qi, Chenguang Lu and Jie Liu, NASA/Rice Workshop on the Growth of nanotubes, April 18, 2007, Burnet, TX,

2. "Single Walled Carbon Nanotubes: from Synthesis to Devices" Jie Liu, Rice University, Department of Chemistry, Feb. 12, 2007, Houston, TX.

3. "Single Walled Carbon Nanotubes: from Synthesis to Devices" Jie Liu, CRANN Seminar Series, Nov. 19, 2006. Trinity College in Dublin, Dublin, Ireland.

4. Controlled synthesis of single walled carbon nanotubes by chemical vapor deposition for nanoscale devices and sensors, Jie Liu, 232nd ACS National Meeting, September 10–14, 2006, San Francisco, CA.

5. Understanding the Relationship between the Growth Conditions and the Diameter of Single Walled Carbon Nanotubes; Jie Liu, FACSS 2006 Conference, September 24–26, Orlando, FL.

6. "Single Walled Carbon Nanotubes: from Synthesis to Devices" Jie Liu, Nanocience Workshop at University of Arkansas-Little Rock, May 1–2, 2006, Little Rock, AR.

7. "Understanding the Relationship between the Growth Conditions and the Diameter of Single Walled Carbon Nanotubes", J. Liu and C. Lu, 209th ECS Meeting , May 7–May 12, 2006, Denver, CO.

References

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2. Z. Yang, Y. Xia and R. Mokaya, Enhanced Hydrogen Storage Capacity of High Surface Area Zeolite-like Carbon Materials, JACS, 129, 1673-1679 (2007).

3. F. H. Yang, A. J. Lachawiec, and R.T.Yang, Adsorption of spillover hydrogen atoms on single-wall carbon nanotubes. Journal of Physical Chemistry B, *110:* 6236-6244, 2006.

4. A.J. Lachawiec, G.S. Qi, and R.T. Yang, Hydrogen storage in nanostructured carbons by spillover: Bridge-building enhancement. Langmuir, *21:* 11418-11424, 2005.

5. J. Miyamoto, et al., Efficient H_2 Adsorption by Nanopores of High-Purity Double-Walled Carbon Nanotubes JACS 128, 12636 (2006).