IV.C.1i Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

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Contract Number: DE-FC36-05GO15073

Start Date: February 1, 2005
Projected End Date: January 31, 2010

Partner Approach

To meet DOE hydrogen storage targets, the key objective is the development of scalable processes that can cost-effectively produce carbon-based materials on a commercial scale. Thus, Rice University will continue developing the quality and characteristics of single-wall carbon nanotubes (SWNTs) as needed for nanoengineering applications. We will also develop processing and chemical treatments of SWNTs that permit 3-D nanoengineering of SWNTs such that pore size is optimized for H_2 storage.

Partner FY 2006 Results

- **SWNT Regrowth:** Developed SWNT growth techniques that enable exact duplication with high yields of desired nanostructures. This has been demonstrated by the further growth of SWNTs whose ends reside at the end of a cut fiber (see Figure 1).
- **3D NanoEngineering:** Outlined processing steps that create nanostructured materials with the optimum pore sizes (geometries) needed for maximum hydrogen storage capacity. Chemical processes for nanoengineering of SWNTs that enable optimum nanostructured materials (e.g. Figure 2) to be held in space with essentially 100% available surface area (>2,300 m^2/g) for maximum gravimetric and volumetric hydrogen storage capacities have been outlined. Space molecules such as bi-phenyl groups will be chemically attached to adjacent SWNTs so as to create a well defined spacing between SWNTs. Different chemical groups will be inserted to give different pore spacings.
- **Aligned SWNT Arrays:** Developed additional nanotube production methods for various types of carpet growth, also known as vertically aligned single wall carbon nanotube arrays. Nanotubes show excellent uniaxial thermal conductivity, nearly that of diamond, and these carpet nanotubes, hundreds of micrometers long, will likely be the best. Because the SWNT are well aligned carpets (as is the case for aligned SWNT fiber) they are a good candidate for nanopore engineering of SWNT spacing such that maximum surface area is created

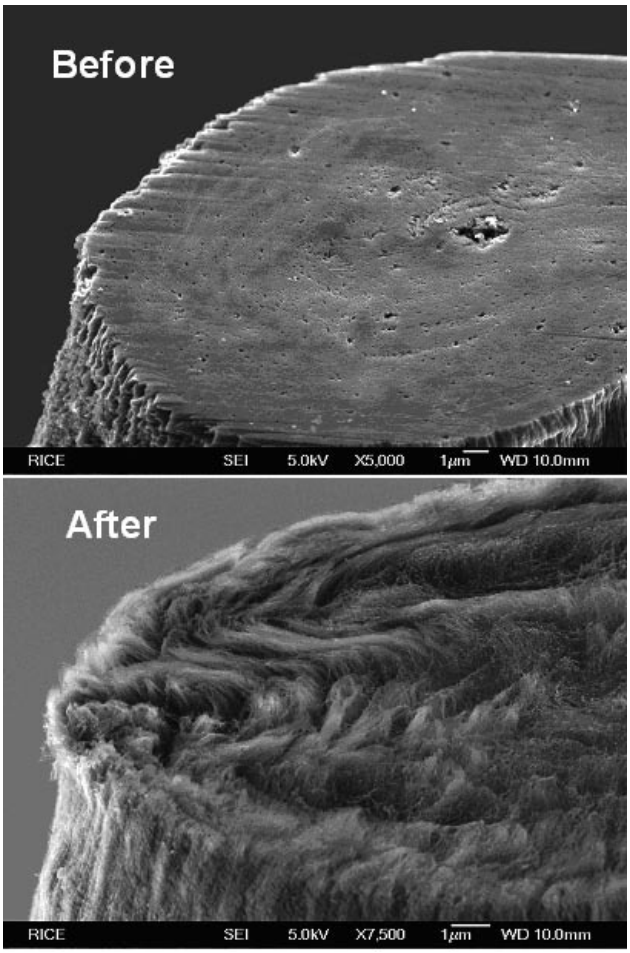

FIGURE 1. SWNT Restarted Growth at the end of a Cut Fiber

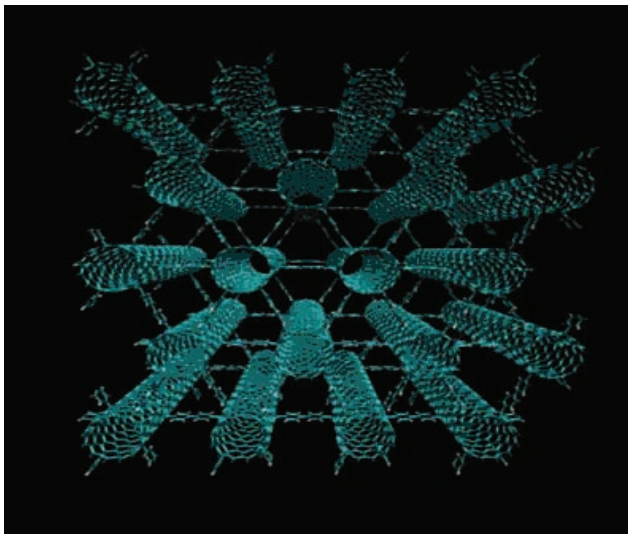

FIGURE 2. Illustration of a SWNT Array Expanded With a Molecular Crosslinker

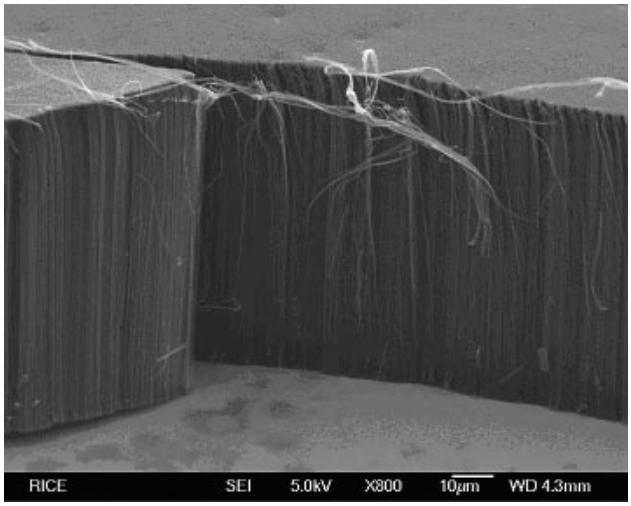

FIGURE 3. TEM Picture of Aligned SWNT

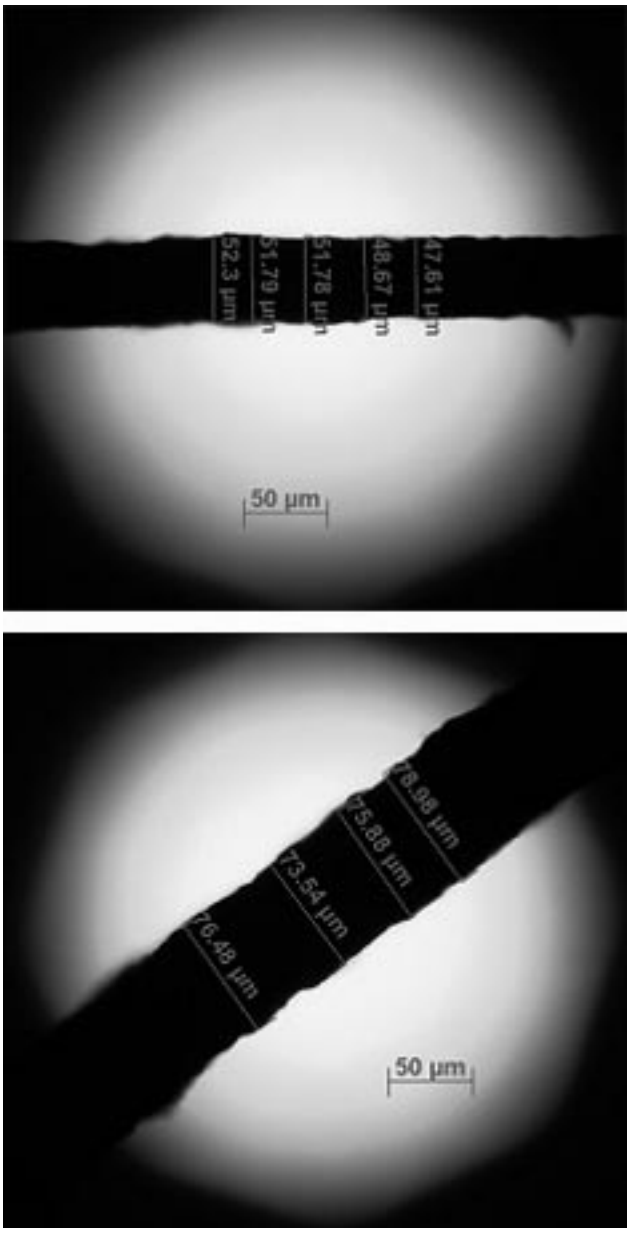

FIGURE 4. Fiber Before (~51 μm) and After (~76 μm) Swelling in Acid and Cross Linking With a Molecular Species, Showing the Fiber has Permanently Expanded by 50%.

in the smallest possible volume. Figure 3 shows an aligned SWNT array.

- **SWNT Fiber:** SWNT fibers were shown to readily swell in 100% sulfuric acid. This increased spacing between SWNT permits molecular spacers to be placed between the SWNT such that when the acid is removed the lattice remains expanded with spacing dimensions set by the molecular spacer. Spun fibers were arrayed into aligned bundles to preserve the uniaxial thermal transport exhibited by individual SWNTs. This fibrous media also provides good gas transport along the axis. The loss of thermal conductivity typical of granular media is mitigated. Figure 4 shows a fiber before and after swelling in acid with crosslinking to make the expansion permanent.. This corresponds to the pore size between nanotubes increasing from 0.34 nm to 0.9 nm.
- **Ozone treated SWNT:** SWNTs were treated with ozone to cut and open up holes in the sidewalls. Ozone treatment increased the surface area from ~600 m^2/g to 1,050 m^2/g. Hydrogen adsorption studies indicated that the sample can adsorb as much as 3 wt% hydrogen at 77 K when the hydrogen pressure is increased to 30 atm. A plot of the hydrogen adsorption data is shown in Figure 5.

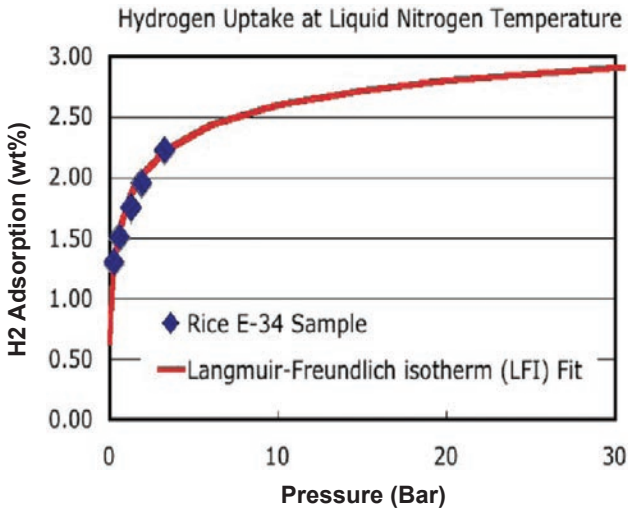

FIGURE 5. Hydrogen Uptake Data for Ozone Treated Sample

Partner FY 2007 Plans

FY 2006 studies indicate that the sample surface area of SWNT materials should be increased to its maximum possible value by expanding the lattice with molecular spacers between all SWNTs. In addition, the spacing between SWNTs should be optimized for maximal hydrogen storage. Theory has suggested a spacing of ~9 angstroms is near the optimum.

- Develop methods for varying the 3-D spacing of the nanoframe. This will involve developing chemical methods for placing molecular spacer between nanotubes. The spacers are expected to take up less than 10% of the available surface area.
- Measure H_2 uptake of new 3-D nanoengineered structures: candidate samples will be measured for Bruner-Emmett-Teller surface area and then sent to NREL for hydrogen uptake measurements.
- Begin (parametric) studies of pore size vs. hydrogen uptake: spacer groups such a condensed ring aromatics, C_{60} carboranes etc will be investigated.
- Adapt 3-D nanoengineering methodology to carpet grown fibers.
- Develop lithium: SWNT atom intercalation methodology whereby the nanoframe is a scaffolding for room temperature uptake of hydrogen onto the lithium (Kubas complex), for which theory predicts over 6 wt%.and 55 g/L.
- Our goal is to achieve uptake of 6 wt% and 45g/L with these different materials.

FY 2006 Publications/Presentations

1. DOE FreedomCar Tech Team Meeting, Washington, D.C., March 2006.

2. DOE FY 2006 Annual Merit Review, Arlington, VA, May 2006.

3. "Single Wall Carbon Nanotube Amplification: A Type-Specific Growth Mechanism", Richard E. Smalley, Yubao Li, Valerie C. Moore, B. Katherine Price, Ramon Colorado, Jr., Howard K. Schmidt, Robert H. Hauge, Andrew R. Barron and James M. Tour, submitted to J. Am. Chem. Soc.

4. "Vertical Array Growth of Small Diameter Single-Walled Carbon Nanotubes", Xu, Y. Q.; Flor, E.; Kim, M. J.; Hamadani, B.; Schmidt, H.; Smalley, R. E.; Hauge, R. H., Journal of the American Chemical Society 2006, 128, (20), 6560-6561.

5. "Effect of Atomic Hydrogen and Active Carbon Species in the 1mm Vertically Aligned Single-Walled Carbon Nanotubes Growth", Ya-Qiong Xu, Erica Flor, Howard Schmidt, Richard E. Smalley, and Robert H. Hauge, (accepted by Appl. Phys. Lett. 2006).

6. "Cutting of SWNTs by Ozonolysis", Chen, Z. Y.; Ziegler, K. J.; Shaver, J.; Hauge, R. H.; Smalley, R. E., Journal of Physical Chemistry B 2006, 110, (24), 11624-11627.

7. "Controlled oxidative cutting of SWNTs", Ziegler, K. J.; Gu, Z. N.; Peng, H. Q.; Flor, E. L.; Hauge, R. H.; Smalley, R. E., Journal of the American Chemical Society 2005, 127, (5), 1541-1547.

8. "Cutting single-walled carbon nanotubes", Ziegler, K. J.; Gu, Z. N.; Shaver, J.; Chen, Z. Y.; Flor, E. L.; Schmidt, D. J.; Chan, C.; Hauge, R. H.; Smalley, R. E.," Nanotechnology 2005, 16, (7), S539-S544.

9. "Individualized SWNTs from Bulk Material Using 96% Sulfuric Acid as Solvent", Stephenson, J. J.; Hudson, J. L.; Azad, S.; Tour, J. M. Chem. Mater. 2006, 18, 374-377.