IV.C.1g Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

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Projected End Date: Project continuation and direction determined annually by DOE

Partner Approach

The purpose of this work is to synthesize and process single-walled carbon nanohorns (SWNHs) as a novel form of nanostructured carbon with tunable pore sizes to optimize the storage of hydrogen and serve as metal catalyst supports for catalyst-assisted hydrogen storage. The shape and size of the individual nanohorns as well as their interstitial pore sizes in their aggregates can be changed by varying their synthesis conditions and by post-processing chemical treatments. Therefore, these novel nanostructures can be nano-engineered and adjusted for optimal hydrogen uptake to maximize supercritical hydrogen adsorption and metal-catalyzed "spillover".

To control the pore sizes in SWNHs, the nanohorn formation mechanisms are understood and controlled using *in situ* process diagnostics (Figure 1). Post-processing and multiple characterization techniques are also developed to control pore size, surface area, defects, and metal nanoparticle decoration. Decorated and undecorated nanohorns are characterized by nuclear magnetic resonance (NMR), neutron scattering, and hydrogen adsorption to reveal the mechanisms of storage for well-characterized samples and to tune synthesis and processing conditions to achieve DOE gravimetric and volumetric hydrogen uptake goals.

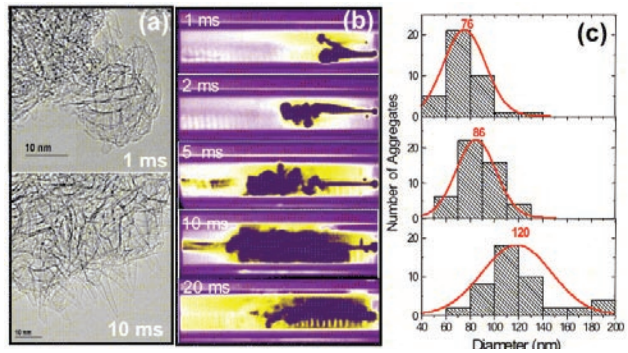

FIGURE 1. The morphology of single-wall carbon nanohorns (SWNHs) can be controlled by changing laser pulse width. (a) TEM images of SWNHs produced at 1 ms and 10 ms. (b) Images of laser ablation plumes. (c) Size distributions of SWNHs aggregates produced at different laser pulse widths.

Partner FY 2006 Results

Research in FY 2006 concentrated mainly upon two tasks:

1. Developing methods for the laser synthesis of gram quantities of pure SWNHs and metal decorated SWNHs, and the development of methods to control the morphology of the nanohorns, through an understanding of their synthesis process.
2. Developing methods to post-process SWNHs to increase their surface area, tune their pore sizes, explore treatments to alter their graphitic structure, methods to chemically decorate nanohorns with metal catalyst nanoparticles, and gain preliminary understanding of which treatments result in increased hydrogen uptake via measurements at our partners facilities.

As a result of work during FY 2006, a high temperature laser ablation approach capable of producing ~9 g/hour of pure and metal decorated SWNHs was developed. *In situ* diagnostics including high-speed videography of the synthesis process, fast pyrometry of the graphite target, and differential mobility analysis monitoring of particle size distributions were applied to understand growth times and control SWNH morphology. Modeling of the heat transfer was performed to achieve uniform target erosion to enable synthesis of gram quantities of SWNHs. Chemical oxidation and other chemical processes were developed to open and decorate SWNHs with metal catalysts such as Pt (Figure 2). *Ex situ* characterization methods, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal gravimetric analysis

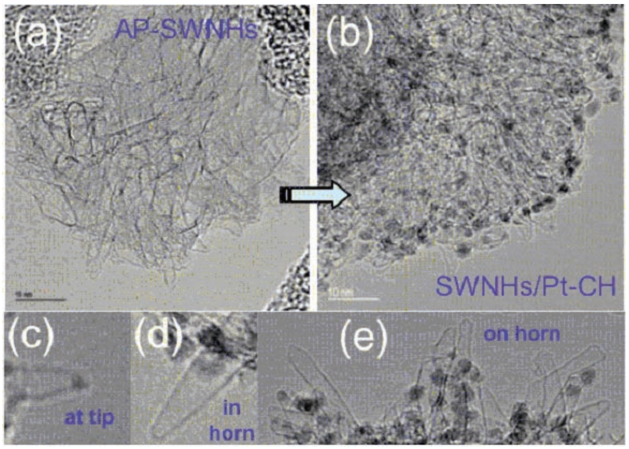

FIGURE 2. TEM images of as-prepared single-wall carbon nanohorns (AP-SWNHs) (a) and Pt nanoparticle decorated SWNHs (SWNHs/Pt-CH) via wet chemical method (b-e).

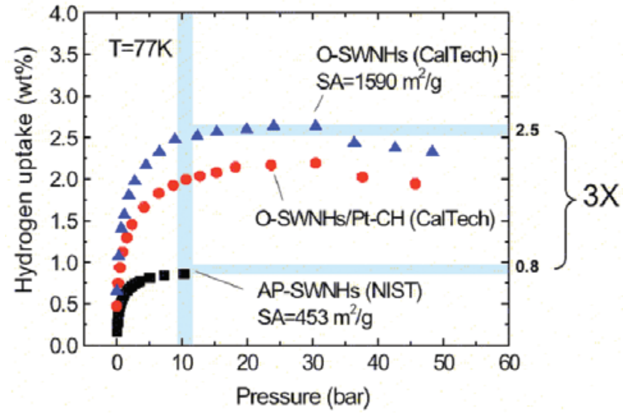

FIGURE 3. Hydrogen isotherm comparisons on as-prepared SWNHs (AP-SWNHs), opened SWNHs (O-SWNHs), and Pt decorated O-SWNHs (O-SWNHs/Pt-CH) via wet chemical method. O-SWNHs (surface area 1,590 m^2/g) have three times the uptake of AP-SWNHs (surface area 453 m^2/g).

(TGA), and Raman spectroscopy were established to characterize as produced and post-processed SWNHs. Initial hydrogen uptake measurements, neutron scattering, and NMR measurements were carried out by CbHS CoE partners (NREL, Air Products, NIST, and CalTech) using as-produced, metal decorated, and chemically modified SWNHs. The highest surface area of opened SWNHs obtained so far is 1,892 m^2/g. Hydrogen uptake measurements show a threefold increase in hydrogen adsorption on chemically processed nanohorns (Figure 3). Neutron vibrational spectroscopy performed at NIST reveals clear evidence for spillover on metal decorated nanohorns. These findings will be clarified in FY 2007.

Partner FY 2007 Plans

Research in FY 2007 will be based on our achievements in FY 2006. The ability to tune the porosity, surface area, and nanostructure of the nanohorns demonstrated both during (a) synthesis and (b) post-processing will be utilized to focus on which pores are storing hydrogen at sufficient densities to meet DOE goals. Varying the synthesis conditions will produce materials with different internal to external pore ratios, producing a rich variety of starting materials. For each, chemical processing treatments demonstrated in FY 2006 will be applied to further modify surface area and pore size. The as-produced nanohorns will be opened to assess the fraction of hydrogen stored in each. Metal decorated unopened, and metal decorated opened nanohorns will be assessed for "spillover". However, the basis of this research is supercritical hydrogen adsorption that theoretically will allow us to reach the gravimetric and volumetric DOE targets in hydrogen storage. Work in Japan indicates that nanohorns can store hydrogen at 70 g/L densities in external pores at 77 K, however variation of the nanohorn structure utilizing high temperature synthesis environments and variable laser pulse widths was not explored. Supercritical hydrogen adsorption or promotion of hydrogen cluster formation in external SWNH nanopores of particular sizes will be explored using nano-engineered pores to induce hydrogen cluster formation at 77 K and higher temperatures. The tunable porosity of the medium, coupled with the freedom to decouple internal and external pores, as well as the level of metal loading (starting at zero), make SWNHs a key test bed for determining hydrogen storage mechanisms in nanoporous carbons. The feasibility of enhancing hydrogen physisorption by stabilizing supercritical hydrogen clusters in different pore sizes and with different dopants will be assessed through theoretical input and simulations by partners in the Center.

ORNL FY 2006 Publications/Presentations

1. "Decoration of Single-wall Carbon Nnanohorns with Metal nanoparticles for Hydrogen Storage", H. Hu, B. Zhao, A. A. Puretzky, D. Styers-Barnett, C. M. Rouleau, H. Cui and D. B. Geohegan, Materials Research Society Spring Meeting, San Francisco, CA, April 17-22, 2006.

2. "Synthesis of Single Wall Carbon Nanotubes and Carbon Nanohorns by High Power Laser Vaporization", D. B. Geohegan, A. A. Puretzky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, I. N. Ivanov, P. F. Britt, APS March Meeting 2006, Baltimore, MD, March 13-17, 2006.

3. "Synthesis of Single Wall Carbon Nanotubes and Carbon Nanohorns by High Power Laser Vaporization", A. A. Puretzky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, Z. Liu, I. N. Ivanov, P. F. Britt, and D. B. Geohegan, Photonics West, SPIE, Conference 6106B, Synthesis and Photonics of Nanoscale Materials, San Jose, California, January 21-26, 2006.

4. "In situ Investigations of Single Wall Carbon Nanohorn Synthesis by High Power Laser Vaporization," D. B. Geohegan, A. A. Puretzky, D. Styers-Barnett, H. Hu, C. M. Rouleau, H. Cui, Z. Liu and B. Zhao, Materials Research Society Fall Meeting 2005 Symp. A10, Boston, MA, Dec. 2, 2005.

5. "Decoration of Single-wall Carbon Nanohorns with Pt Nanoparticles", H. Hu, B. Zhao, A. A. Puretzky, D. Styers-Barnett, C. M. Rouleau, H. Cui and D. B. Geohegan, Materials Research Society Fall Meeting 2005 Symp. A10, Boston, MA, Dec. 2, 2005.

6. "Time-Resolved Measurements of Nanotube and Nanohorn Growth", D. B. Geohegan, A. A. Puretzky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, I. N. Ivanov, P. F. Britt, SESAPS Annual Meeting 2006, Williamsburg, VA, November 2005.

7. "Synthesis of Functional Single Wall Carbon Nanohorns and Nanotubes by High Power Laser Vaporization", D. B. Geohegan, A. A. Puretzky, H. Cui, H. Hu, C. M. Rouleau, Z. Liu, D. Styers-Barnett, I. N. Ivanov, and B. Zhao, The 8th International Conference on Laser Ablation, Banff, Canada, September 11-16, 2005.