IV.C.1k ORNL Progress within the DOE Center of Excellence for Hydrogen Sorption: Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

David B. Geohegan (Primary Contact), Mina Yoon, Alex A. Puretzky, Christopher M. Rouleau, Hui Hu, Bin Zhao, and Karren More

Oak Ridge National Laboratory (ORNL)
Materials Science and Technology Division
and the Center for Nanophase Materials Sciences
1 Bethel Valley Road, MS-6056
Oak Ridge, TN 37831-6064
Phone: (865) 576-5097; Fax: (865) 574-1753
Email: geohegandb@ornl.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: carole.read@ee.doe.gov

Subcontractor:
Oak Ridge Institute for Science and Education,
Oak Ridge, TN

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

Objectives

Exploit the tunable porosity and excellent metal supportability of single-walled carbon nanohorns (SWNHs) to optimize hydrogen uptake and binding energy:

- Optimize morphologies of SWNHs by adjusting their pore sizes and by increasing their surface area.
- Quantify hydrogen storage capacity of SWNHs aggregates as a function of their morphology changes.
- Theoretically understand interactions between different coating metals and hydrogen. Search for the coating element which generate effective hydrogen binding sites and minimizes metal clustering on nanostructured carbon surfaces.
- Develop new synthesis/decoration approaches to synthesize theoretically predicted materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is developing nanoengineered metal-decorated carbon nanohorns for use as effective hydrogen storage media to satisfy DOE system targets. The project is addressing the 2010 system targets of:

- System Gravimetric Capacity: 2 kWh/kg (0.06 kg H_2/kg system)
- System Volumetric Capacity: 1.5 kWh/L (0.045 kg H_2/L system)
- Charging/Discharging Rates: 3 min for 5 kg system fill

Currently, this project has demonstrated gravimetric hydrogen uptakes of SWNHs between 0.6-1.5 wt% at room temperature, ~3.5 wt% at 77 K, and ~6.4 wt% at 30 K. The volumetric capacity demonstrated to date is 30 g/L for compressed pellets of decorated, opened nanohorns which is 67% of the 2010 system target. This project will also address the high thermal conductivity requirements required for system charging through incorporation of high thermal diffusivity (2.1 cm^2/s) porous aligned nanotube arrays with the nanohorn storage medium.

Accomplishments

- **Synthesis:** SWNHs with tunable morphologies were synthesized at scalable production (10 g/hr rates) and decorated with Pt and Pd nanoparticles with controllable weight loadings (from 3 wt% to 20 wt%). Pellets of metal-decorated nanohorns can be compressed to the volumetric density of 30 g/L.
- **Processing:** Surface area of nanohorns was significantly improved to 2,200 m^2/g. The pore sizes were controlled from 1.7 nm to below 1 nm using softer oxidative (CO_2) chemistry and the pore

size distributions, nanostructure morphologies, and graphitic content were characterized. Their effects on surface area and uptake were investigated.

- **Hydrogen Uptake** of ~3.5 wt% at 77 K and ~6.4 wt% at 30 K was measured for nanohorns with tailored pores (<1 nm) having surface areas of 2,200 m^2/g. Significant room temperature storage (~0.6 wt% at 30 bars) better than that of bridged MOF-177 (metal organic framework, MOF) at the same pressure.
- **Theory and Modeling:** The strong binding of hydrogen due to metal decoration was investigated theoretically and the optimal materials (alkaline earth metals) which avoid clustering on carbon supports, yet provide a dipole-induced polarization and binding of molecular hydrogen sufficient to meet DOE targets, were predicted.
- **Synthesis of New Materials:** Theoretical study shows that Ca-decorated carbon structures have a high hydrogen storage capacity (~8.4 wt%) with binding energy of 0.4 eV per hydrogen molecule. Experimental techniques were developed and implemented to synthesize these theoretically predicted structures, namely homogeneously Ca-decorated SWNHs.

Introduction

The purpose of this project is to synthesize functionalized SWNHs for use as a high capacity hydrogen storage media which satisfies DOE technical targets. Nanohorns are cone-shaped, atomic-layer-thick nanostructures which contain preferred hydrogen adsorption sites in their tips and have variable internal and interstitial pores that have been shown to contain hydrogen at liquid hydrogen density or higher. They can be functionalized by tailoring their pores, their surface area, and by metal decoration. They are very promising nanoporous materials for hydrogen storage, can be produced in large quantities, and have been shown to serve as excellent metal catalyst supports for fuel cells and batteries in addition to their potential as sorbents.

The ultimate goal of this project is to make use of SWNH complexes for efficient hydrogen storage media by (a) utilizing their high surface areas effectively to meet hydrogen gravimetric DOE targets, (b) optimizing their geometries for containing high volumetric densities of hydrogen, and (c) increasing their binding strength to hydrogen by metal decoration for ambient condition hydrogen storage application. In order to satisfy this goal we:

- Developed techniques to control the morphology and metal loading of SWNH composites both during synthesis, and subsequent processing.
- Developed theoretical predictions and experimental methods for metal-decorated carbon nanostructures which can bind hydrogen by utilizing the entire surface area of the nanohorn aggregates through theoretical calculations and computer simulation followed by controlled experiments.

Approach

During laser ablation of carbon or carbon/metal targets, the processing environment is controlled using in situ process diagnostics to tune the individual nanohorn structure. Architectures of these individual nanostructures are assembled from the *"bottom up"* forming a unique nanoporous material. Activation and etching of the nanohorn architectures is used to change the internal:external pore ratios and adjust the interstitial pores. Nanohorn chemistry and processing treatments (heat, compression) are then applied to further tailor the pore size, surface area, and chemical functionality through the introduction of defects. Wet chemistry or vapor infiltration techniques are applied to deposit metal atoms and clusters directly on (or inside) the nanohorns. These controllably decorated nanohorns with metal clusters for enhanced hydrogen storage (Figure 1) are well characterized by transmission electron microscopy (TEM), scanning electron microscopy, Raman, thermogravimetric analysis, Brunauer-Emmett-Teller, temperature programmed desorption (TPD), neutron scattering, nuclear magnetic resonance (NMR), and hydrogen adsorption to understand dominant hydrogen adsorption mechanisms. Theoretical calculations and model simulations are coordinated with experiments to understand the role of metal atoms in enhancing

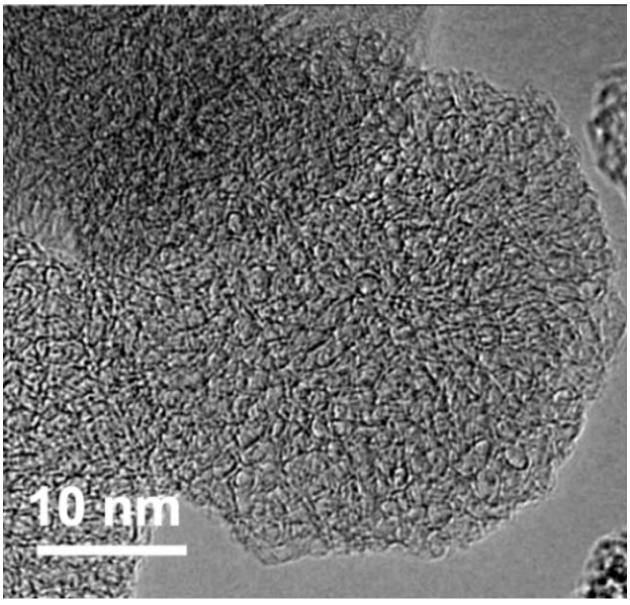

FIGURE 1. TEM Image of SWNH Aggregates Decorated with Pt Nanoparticles

adsorption and binding energy, and to predict new materials and mechanisms to achieve DOE targets.

Results

Shorter laser pulse widths and softer oxidative (CO_2) postprocessing chemistry were developed to increase pore volumes (from 1.3 ml/g to 1.6 ml/g), increase processing yield (from 30% to 70%), and improve the surface area of the materials to 2,200 m^2/g. Nanohorn pore sizes were tuned from 1.7 nm to below 1 nm by post-synthesis processes such as oxidation, compression, and thermal treatments. By engineering the nanohorn unit size to small dimensions, an activated (pure carbon nanohorn) medium with sub-nanometer pores was made which exhibits significant room temperature storage (0.6 wt% at 30 bars). This result is better than that of bridged MOF-177 at the same pressure (Figure 2). Wet chemical deposition processing, which was developed in Fiscal Year 2007, was employed to decorate SWNHs with Pt and Pd nanoparticles with controllable weight loadings (from 3 wt% to 20 wt%) to study the spillover mechanism, metal clustering behavior, and metal-hydrogen interactions in collaboration with Hydrogen Sorption Center of Excellence partners.

Effects of metal decoration on SWNHs indicate spillover in both Pt- and Pd-decorated SWNHs as observed by neutron scattering monitoring of free H_2 by the National Institute of Standards and Technology with an onset temperature 150 K < T < 298 K. In addition, several measurements showed increased binding energy and room temperature storage in Pt-decorated SWNHs (NMR [7.1 kJ/mol, University of North Carolina, UNC]), TPD [36 ± 2 kJ/mol, National Renewable Energy Laboratory, NREL]). Hydrogen storage measurements by Caltech, NIST, NREL and UNC demonstrated hydrogen uptakes of SWNHs with 0.2-0.8 wt% at room temperature and 1-3.5% at 77 K. Our theoretical studies of metal decoration investigate charge redistribution of the system as a mechanism for increased hydrogen binding. Our study shows that charged nanostructures can generate good and tunable hydrogen binding sites (e.g. a charged fullerene, C_{82}^{+6} can bind 8.0 wt% of hydrogen molecules with ~0.3 eV/H_2) due to polarization of hydrogen molecules by the high surface electric fields generated by charging. The electric field resulting from just a few surface charges on nanoscale materials is sufficient for significant hydrogen storage.

Using computational calculations based on first principles density functional techniques, a search for an alternative coating element was performed which could generate strong hydrogen binding sites and structures and would be stable against metal clustering. Ca was found to be superior due to the unique binding mechanism of Ca to nanoscale carbon materials. Predictions of perfectly coated C nanostructures as shown in Figure 3 should be possible, and bind significant (8.4 wt%) hydrogen with significant energy ~0.4 eV/H_2. Experimental efforts have been made in order to implement this theoretical prediction, and Ca-decorated carbon nanohorns were verified using high-resolution TEM and energy dispersive X-ray, as shown in Figure 4. Higher magnification TEM images indicate

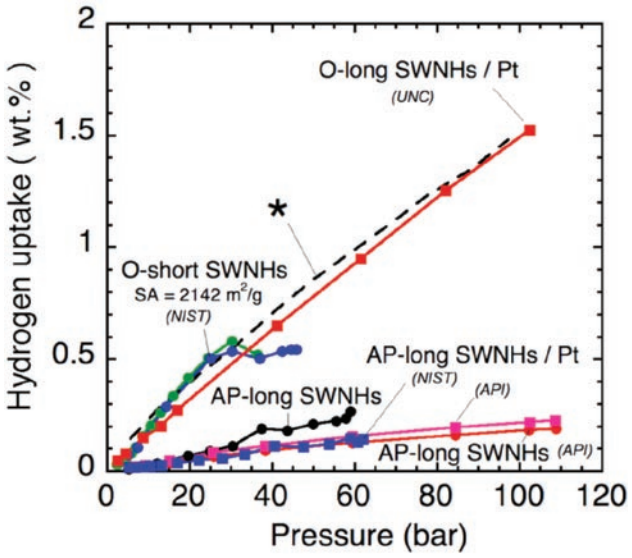

FIGURE 2. Room-temperature hydrogen uptake improvements for opened short, SWNHs (O-short SWNHs) as compared to AP (as produced) long and short SWNHs, with and without Pt decoration. The undecorated, O-short SWNHs follow the same trend as bridged MOF-177 [dashed line * - spillover material reported by R. Yang, et al. Langmuir 23, 12937 (2007)] and exceed the Pt-decorated, O-long SWNHs produced at ORNL.

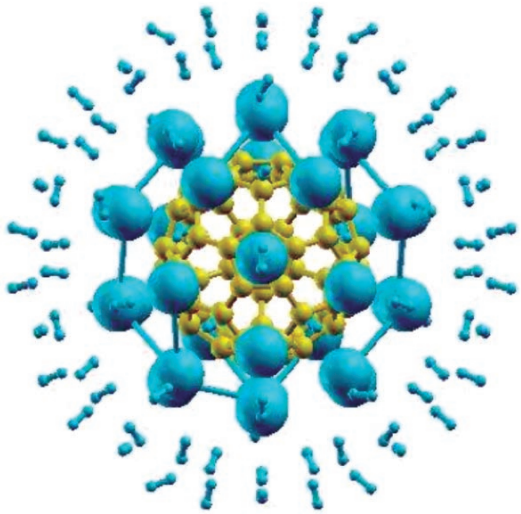

FIGURE 3. First principles calculations optimization for a Ca-decorated C_{60} predicts 32 bound Ca atoms and adsorption of 92 H_2 molecules due to charge-induced polarization, corresponding to a hydrogen uptake of 8.4 wt%.

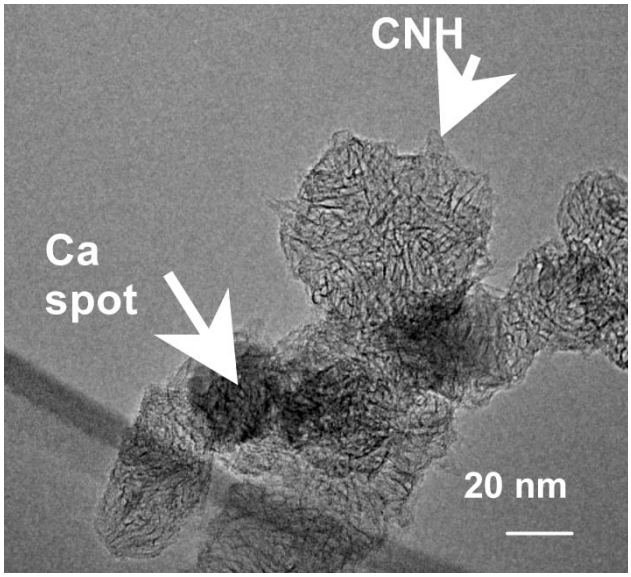

FIGURE 4. TEM Image of Ca-Decorated SWNHs

possible interstitial Ca intercalation, as evidenced by interwall spacings of ~0.4 nm between the walls of the nanohorns within the aggregates.

Conclusions and Future Directions

With HSCoE partners, results showed that metal-decorated SWNHs exhibit increased binding energy, spillover, and anomalous room-temperature storage. Two important results from this year's effort provide a path forward for the project in FY 2009 and beyond.

- First, engineering the nanohorn unit size to small dimensions yielded an activated (pure carbon nanohorn) medium with sub-nanometer pores which exhibits significant room temperature hydrogen storage (0.6 wt% at 30 bars). Efforts will be made to further optimize the nanostructure and activated architectures to enhance binding energy at tailored sites.
- Second, theoretical investigations yielded significant progress toward understanding the strong binding of hydrogen due to metal decoration. Calculations predicted the optimal material (Ca) to decorate carbon nanostructures and bind molecular hydrogen using dipole-induced polarization by high, local electric fields. Efforts will focus on confirming these predictions, and producing these optimally-decorated nanostructures for testing by HSCoE partners. Continued investigation of the spillover mechanism will continue.
- New C nanostructures and nanocomposites will be explored to provide auxiliary materials with enhanced binding sites and thermal management to support DOE targets.

Special Recognitions & Awards/Patents Issued

1. An invention disclosure "Hydrogen Storage on Ca Doped Nanostructures" was submitted by Mina Yoon, Shenyuan Yang, Zhenyu Zhang, and David Geohegan.

FY 2008 Publications/Presentations

1. *"Calcium as a superior coating metal in functionalization of carbon fullerenes for high-capacity hydrogen storage"* M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang (Phys. Rev. Lett. 100, 206806 (2008).

2. *"High Power Laser Vaporization Synthesis of Single Wall Carbon Nanotubes and Nanohorns"* A.A. Puretzky, D.B. Geohegan, D. Styers-Barnett, C.M. Rouleau, B. Zhao, H. Hu, M.D. Cheng, D.W. Lee, I.N. Ivanov *Appl. Phys. A (published on line*: http://dx.doi.org/10.1007/s00339-008-4744-3*)*.

3. *"In situ time-resolved measurements of carbon nanotube and nanohorn growth"*, D.B. Geohegan, A.A. Puretzky, D. Styers-Barnett, H. Hu, B. Zhao, H. Cui, C.M. Rouleau, G. Eres, J.J. Jackson, R.F. Wood, S. Pannala, J. Wells *phys. stat. sol. (b)* 244, No. 11, 3944 (2007).

4. *"Formation studies and controlled production of carbon nanohorns using continuous in situ characterization techniques"* Meng-Dawn Cheng, Doh-Won Lee, Bin Zhao, Hui Hu , David J Styers-Barnett, Alexander A. Puretzky, David W DePaoli, David B Geohegan, Emory A Ford and Peter Angelini *Nanotechnology* 18, 185604 (2007).

5. *"Charged Fullerenes as High-Capacity Hydrogen Storage Media"* Mina Yoon, Shenyuan Yang, Enge Wang, Zhenyu Zhang, *Nano Letters* 7, 2578 (2007).

6. *"Tailoring of Single Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports"* Hui Hu, Bin Zhao, Alex A. Puretzky, Chris M. Rouleau, David Styers-Barnett, David B. Geohegan, Craig M. Brown, Yun Liu, Wei Zhou, Houria Kabbour, Dan A. Neumann, and Channing Ahn - *Proceedings of Carbon 2007 - Seattle, WA*.

7. *"Light Alkaline-Earth-Metal Coated Carbon Fullerenes as Effective Hydrogen Storage Media"* Mina Yoon, Shenyuan Yang, Christian Hicke, Enge Wang, David Geohegan, Zhenyu Zhang at the 2008 Material Research Society Spring Meeting, San Francisco, CA, March 26, 2008, oral presentation.

8. *"Light Alkaline-Earth-Metal Coated Carbon Fullerenes as Effective Hydrogen Storage Media"* Mina Yoon, Shenyuan Yang, Christian Hicke, Enge Wang, David Geohegan, Zhenyu Zhang at the 2008 March Meeting of the American Physical Society, New Orleans, LA, March 12, 2008, oral presentation.