IV.C.1l ORNL Progress within the DOE Center of Excellence for Hydrogen Sorption: Synthesis and Processing of Single-Wall Carbon Nanohorns for Metal-Catalyst Assisted Hydrogen Storage

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Project Start Date: FY 2005
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Synthesize and process carbon single-wall nanohorns (SWNHs) as tailorable nanoporous media with controllable metal decoration for metal-assisted hydrogen storage by:
  - Tailoring the morphology of the individual nanohorn units during synthesis,
  - Further adjustment of the surface area and pore size distributions by controllable post-processing treatments, and
  - Optimized metal decoration.
- Understand dominant mechanisms for hydrogen storage through collaborations with center partners.
- Development of new methods to enhance hydrogen binding energy which utilize the full surface of the sorbent through coordinated theory, modeling, and experiments.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section 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
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

Carbon-Based Materials and other High Surface Area Sorbents

This project is developing synthesis and processing approaches for loose single-wall nanoporous carbons with tunable porosity to match the optimal pore sizes and surface areas predicted by theory to result in maximal hydrogen storage. The project is exploring the fundamental mechanisms of hydrogen storage through controllable decoration of SWNHs with metal catalysts to probe how adsorption of metal clusters increases binding energy and permits utilization of the entire sorbent surface area. 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 minutes for 5 kg system fill

Currently, this project has demonstrated gravimetric hydrogen uptakes of SWNHs between 0.2-0.8 wt% at room temperature and 1-3.5% at 77 K. Thus, at 77 K we are roughly halfway to the 2010 system target and the enhanced binding energies measured to date promise to result in increases in hydrogen storage capacities at higher temperatures through future work. 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 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 and processing of SWNHs were performed to construct a new form of metal-decorated nanoporous carbon with tunable pore sizes and high surface areas to optimize hydrogen storage. Processing treatments, theory, and modeling were also performed to enhance the binding energy of hydrogen and to explore the mechanisms of hydrogen storage in collaboration with Hydrogen Sorption Center of Excellence (HSCoE) partners.

- **Synthesis**: SWNHs with controllably variable morphology were synthesized at 10 g/hr rates by a laser vaporization process to explore the optimal pore sizes for enhanced binding energies of H_2.
- **Processing**: Softer oxidative (CO_2) chemistry was developed to process nanohorns to increase pore volumes (from 1.3 ml/g to 1.6 ml/g), increase processing yield (from 30% to 70%) while maintaining high surface areas (1,900 m^2/g). Post-synthesis adjustment of nanohorn aggregate pore sizes was demonstrated through oxidation, compression, and thermal treatments. Wet chemical deposition processing was developed to decorate SWNHs with Pt and Pd nanoparticles with controllable weight loadings (from 3 wt% to 20 wt%) for supply to HSCoE participants at hundreds of milligram batch quantities.
- **Adsorption**: Hydrogen uptake, neutron scattering, nuclear magnetic resonance (NMR), and temperature programmed desorption (TPD) measurements were performed for metal-decorated SWNHs by HSCoE partners. Evidence for a spillover mechanism in both Pt- and Pd-decorated SWNHs was observed by neutron scattering monitoring of free H_2 losses in decorated vs. undecorated samples. The onset temperature (T) for catalyst-assisted hydrogen storage was determined to be between 150 K<T<298 K. Pt-decorated SWNHs exhibited enhanced binding energies as measured by both TPD (36 ± 2 kJ/mol) and NMR (7.1 kJ/mol).
- **Theory and Modeling**: Theory and modeling approaches were developed to understand the energetics and kinetics of Ti cluster growth on carbon nanostructures in order to develop methods to reduce metal aggregation for new classes of sorption materials with enhanced binding energy. Atomistic modeling was performed to investigate alternative materials to 3d-transition metals which are as light and chemically active, yet have weak intermetallic interactions. Calculations utilizing charged fullerenes as a model system showed up to 8 wt% hydrogen uptake, indicating the important role of surface charge in hydrogen storage.

Introduction

The purpose of this work is to synthesize and process metal-decorated SWNHs as a tailorable nanoporous media for metal-assisted hydrogen storage. Nanohorns are irregular, cone-shaped “bottles” for hydrogen storage which are a single atomic layer thick, and thus a near perfect hydrogen storage medium to maximize surface area. Research has shown that nanohorn pores of critical sizes can store hydrogen at liquid or higher density, however mechanisms to tailor the pore sizes of nanohorns have not been developed due to a lack of knowledge of their formation process. In this project, the morphology and metal loading of SWNH composites are tailored through adjustment of the shape and size of the individual nanohorn units during synthesis, by adjustment of the surface area and pore size distributions of their aggregates by controllable post-processing treatments, and by metal decoration processing treatments. Therefore these novel nanostructures can be nano-engineered and adjusted for optimal hydrogen uptake to maximize supercritical hydrogen adsorption through an understanding of metal-assisted hydrogen storage mechanisms such as spillover and surface charging.

Due to their irregular nanoscale morphology, nanohorns are used to support nanoscale metal catalyst clusters or other materials to form interesting composite structures. Metal catalysts are used not only to dissociate hydrogen, but to assist in the binding of the hydrogen (both atomic and molecular) to the nanohorns’ high surface area support structure. This project investigates ways, through theoretical calculations and computer simulation followed by controlled experiments, of decorating carbon nanostructures with metal atoms, clusters, and other materials to bind hydrogen utilizing the entire surface area of the nanohorn aggregates. Therefore, this project attempts to understand how to simultaneously (a) utilize the high surface areas more effectively to address gravimetric DOE targets, (b) utilize the geometry of the media synthesized in the project to store hydrogen at high volumetric densities, and (c) increase the binding energy of the hydrogen to the media to store hydrogen at elevated temperatures (ultimately room temperature or beyond) to meet key Department of Energy goals.

Approach

During laser ablation of carbon or carbon/metal targets, the parameters of the laser and the processing environment are controlled using *in situ* process diagnostics to tune the individual nanohorn structure and that of their aggregate structures. Materials with varied internal:external pore ratios and interstitial pores can be synthesized. 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 is applied to grow metal clusters directly on (or inside) the nanohorns. These controllably decorated nanohorns with metal clusters for enhanced hydrogen storage are well characterized by transmission electron microscopy, scanning electron microscopy, Raman, thermogravimetric analysis, Brunauer-Emmett-Teller (BET), TPD, neutron scattering, NMR, and hydrogen adsorption to understand dominant hydrogen adsorption mechanisms. Theoretical calculations and model simulations are coordinated with experiments to understand the observed role of metal atoms in enhancing adsorption and binding energy, and to predict new materials and mechanisms to achieve DOE targets.

Results

Research in FY 2007 concentrated upon two tasks: 1) developing controlled synthesis of SWNHs with varied internal:external pore ratios by laser vaporization, and 2) developing controllable processing chemistry to tailor SWNHs pore size, surface area, and metal decoration. Collaborating with center members to investigate the dominant mechanisms of hydrogen storage in metal-decorated nanohorns to address gravimetric and volumetric DOE targets was also undertaken.

As a result of work during FY 2007, SWNHs with tunable morphology were synthesized at multigram scale at ORNL and delivered to participants, along with metal-decorated samples. Softer oxidative (CO_2) chemistry was developed to process nanohorns to increase pore volumes (from 1.3 ml/g to 1.6 ml/g), increase processing yield (from 30% to 70%) while maintaining high surface areas (1,900 m^2/g). Post-synthesis adjustment of nanohorn aggregate pore sizes was demonstrated through oxidation, compression, and thermal treatments. Wet chemical deposition processing was developed to decorate SWNHs with Pt and Pd nanoparticles with controllable weight loadings (from 3 wt% to 20 wt%) for supply to HSCoE participants at hundreds of milligram batch quantities to probe the spillover mechanism and enhance the binding energy for stored hydrogen (Figure 1). Micropore distributions of as-prepared and opened SWNHs by CO_2 and N_2 BET showed multiple pores centered at 0.35, 0.55, 0.82, 1.2, 1.8, 3.0 nm.

Evidence for spillover in both Pt- and Pd-decorated SWNHs was observed by neutron scattering monitoring of free H_2 by the National Institute of Standards and Technology (NIST) (Figure 2). The onset temperature for catalyst-assisted hydrogen storage was determined to be between 150 K< T< 298 K. NMR measurements by the University of North Carolina (UNC) showed

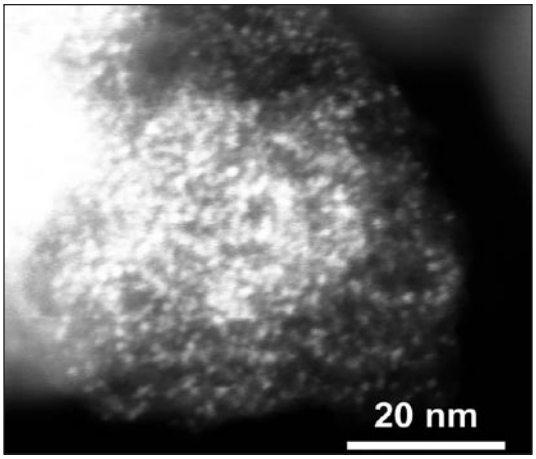

FIGURE 1. Z Contrast Scanning Transmission Electron Microscopy Images of Single-Wall Carbon Nanohorn Aggregates Decorated Controllably with Pt Nanoparticles

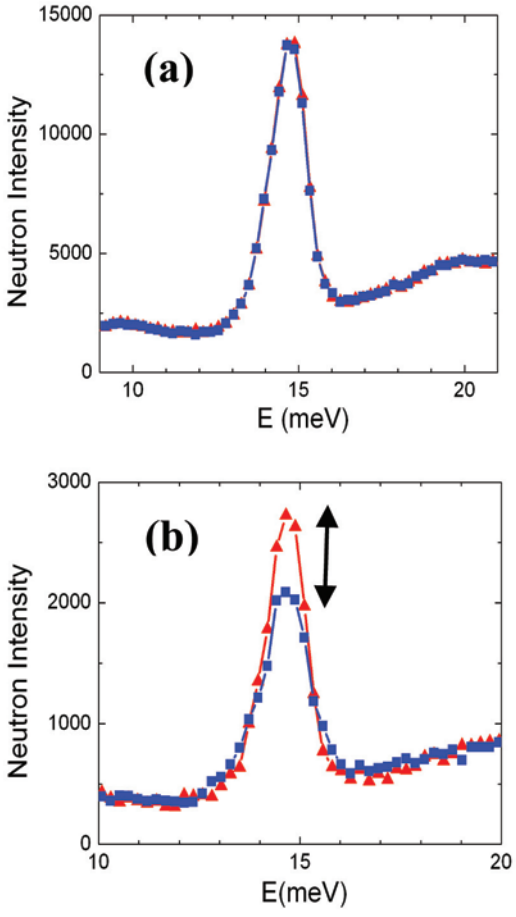

FIGURE 2. Neutron scattering measurements of rotational band of H_2 showing "spillover" losses of H_2 for Pt-decorated SWNHs after heating samples from 77 K (red) to (a) 150 K (blue), (b) 298 K (blue). NIST (unpublished) data Y. Liu, C. Brown, and D. Neumann.

possible spillover-related room temperature storage in Pt-decorated SWNHs. Moreover, Pt-decorated SWNHs exhibited enhanced binding energies as measured by both TPD (36 ± 2 kJ/mol, *National Renewable Energy Laboratory*) and NMR (7.1 kJ/mol, *UNC)*. 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. Theory and simulation of effects of metal decoration on hydrogen binding energy and storage have also been studied to predict enhanced binding energies vs. induced field strength. The effects of compression and thermal treatments to further vary the pore sizes and the graphitic structure of SWNHs was also studied. Theory and modeling efforts at ORNL were devoted to understanding methods and energetics of uniform metal deposition on carbon nanostructures, to explain the role of these metal atoms observed in enhanced adsorption and increased binding energy, and to predict new directions based upon locally charged nanostructures to achieve DOE targets. Calculations utilizing charged fullerenes as a model system showed up to 8 wt% hydrogen uptake, indicating the important role of surface charge in hydrogen storage.

Conclusions and Future Directions

Research with HSCoE partners in FY 2007 described above revealed that metal-decoration of nanohorns results in increased binding energy of hydrogen (TPD and NMR studies), and shows evidence for spillover (neutron scattering and NMR studies). Moreover, significant room-temperature storage was indicated in some NMR experiments. Measurements and techniques developed in this project in FY 2007 now permit the rapid measurement at ORNL of the entire range of (including sub-nm) pore sizes, permitting the optimization of the media through the tunability of pore sizes demonstrated during synthesis and during post processing. Theory developed at ORNL presented an alternate explanation for the interactions of adsorbed metals and other species with nanosized carbons through surface charge-induced hydrogen polarization, providing future directions for experiments to tailor decorated nanohorn composites with high binding energies to meet DOE targets.

Research in FY 2008 will pursue further enhancements in hydrogen storage, building upon discoveries in FY 2007 of increased binding energy, spillover and charging mechanisms, and the ability to tailor SWNH pore sizes and surface areas. The theory and modeling effort will be expanded in FY 2008 to search for alternative materials to 3d-transition metals which are as light and chemically active, yet have weak intermetallic interactions to enable uniform coverage. The nanohorn synthesis will be based on converging theoretical predictions for an optimal

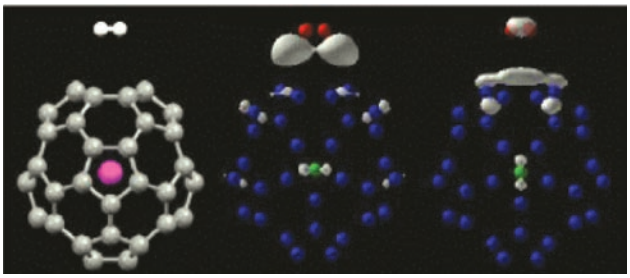

FIGURE 3. Modeling of the Charge Distribution on the Outer Surface of a Fullerene Reveals How Single Metal Atoms of La Inside C_{50} Can Polarize and Bind H_2. (M. Yoon et al., in preparation).

pore size (~0.7 nm) for enhanced binding energy of physisorbed hydrogen (PNAS, 102, 10439 [2005]). New types of doped and metal-decorated SWNHs guided by theoretical calculations will be synthesized, characterized and delivered to our partners to test our theoretical models of hydrogen storage and increased binding energy, which indicate that the surfaces of charged carbon nanostructures are affecting hydrogen storage (Figure 3). Synthesis and post-processing chemistry of the nanohorns will be coordinated to tune the porosity to the optimal size, and increase the surface area to enable meeting DOE targets. We will collaborate with our partners to further understand the "spillover" effect and identify dominant mechanisms responsible for hydrogen storage in metal-decorated samples. New methods to charge nanostructures and to nanoengineer nanostructured composites will be explored.

FY 2007 Publications/Presentations

1. *"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* **2007,**18,185604.

2. *"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, Channing Ahn, Carbon 2007 Conference Proceedings.

3. *"Charged fullerenes as high capacity hydrogen storage media",* Mina Yoon, Shenyuan Yang, Enge Wang, and Zhenyu Zhang *(submitted to Nano Lett. for publication, 2007).*

4. *"Single-walled carbon nanohorns: Tunable media for hydrogen storage and metal nanoparticle decoration"*, Hui Hu, Bin Zhao, Alex A. Puretzky, David Styers-Barnett, Chris M. Rouleau, David B. Geohegan, 233rd ACS National Meeting & Exposition, Chicago, IL, March 25-29, 2007, oral presentation.

5. *"Functionalized carbon nanostructures as potential hydrogen storage media",* Mina Yoon, Shenyuan Yang, Enge Wang, and Zhenyu Zhang, March Meeting of the American Physical Society, Denver, CO, March 6, 2007, oral presentation.

6. *"Interaction of transition metals with carbon nanostructures",* Shenyuan Yang, Mina Yoon, Enge Wang, and Zhenyu Zhang, March Meeting of the American Physical Society, Denver, CO, March 6, 2007, oral presentation.

7. *"The tailoring of single-walled carbon nanohorns for hydrogen storage",* Hui Hu, Bin Zhao, Alex A. Puretzky, David Styers-Barnett, Chris M. Rouleau, and David B. Geohegan, Materials Research Society Fall Meeting, Boston, MA, November 27-December 1, 2006, oral presentation.