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DOE Hydrogen Sorption Center of Excellence: Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

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Executive Summary

The overall objective of the project was to exploit the unique morphology, tunable porosity and excellent metal supportability of single-walled carbon nanohorns (SWNHs) to optimize hydrogen uptake and binding energy through an understanding of metal-carbon interactions and nanoscale confinement.SWNHs provided a unique material to understand these effects because they are carbon nanomaterials which aresynthesized from the "bottom-up" with well-defined, sub-nm pores and consist of single-layer graphene, rolled up into closed, conical,horn-shaped units which form ball-shaped aggregates of ~100-nm diameter. SWNHs were synthesized without metal catalysts by the high-temperature vaporization of solid carbon, so they can be used to explore metal-free hydrogen storage. However, SWNHs can also be decorated with metal nanoparticles or coatings in post-processing treatments to understand how metals augment hydrogen storage.

The project first explored how thesynthesis and processing of SWNHs could be modified to tailor pore sizes to optimal size ranges. Nanohorns were rapidly synthesized at 20g/hr rates by high-power laser vaporization,enabling studies such as neutron scattering with gram quantities.Diagnostics of the synthesis process including high-speed videography, fast pyrometry of the graphite target, and differential mobility analysis monitoring of particle size distributions were applied in this project to provide in situ process control of SWNH morphology, and to understand the conditions for different pore sizes. We conclude that the high-temperature carbon-vaporization process to synthesize SWNHs is scalable, and can be performed by electric arc or other similar techniques as economically as carbon can be vaporized. However, the laser vaporization approach was utilized in this project to permit the precise tuning of the synthesis process through adjustment of the laser pulse width and repetition rate. A result of this processing control in the project was to eliminate the large (2-3 nm) internal pores of typical SWNHs which were found (by NMR studies performed at Univ. of North Carolina) not to store hydrogen effectively.

Post processing treatments of the as-synthesized SWNHs focused on pore size, surface area, and metal decoration in order to understand the effects of each on measured hydrogen uptake. Wet chemistry and gas-phase oxidation treatments were developed throughout the life of the project to adjust the interstitial and slit pore sizes of the as-produced SWNHs, and increase the surface area to a maximum value of 2200 m^2/g. In addition, wet chemistry approaches were used to develop methods to decorate the nanohorns with small Pt and Pd nanoparticles for metal-assisted hydrogen storage. Finally, oxygen-free decoration of SWNHs with alkaline earth metals (Ca) was developed using pulsed laser deposition and vacuum evaporation in order to produce surface coatings with high static electric fields sufficient to polarize and bind dihydrogen.

The bottom-up synthesis of nanohorn aggregates with stable internal pore sizes permitted exploration of tunable interstitial and slit pores on hydrogen sorption. NMR confirmed the majority of storage in the interstitial (~ 0.5 nm) pores on large SWNHs, and in activated pores (< 1 nm) in short-SWNHs. These NMR shifts are the highest among all materials studied, indicating storage in very small pores. Undecorated, short oxidized-SWNHs reversibly store significant hydrogen (0.6 wt.% at 30 bar) at room temperature, comparable to bridged MOFs and Pt-decorated O-SWNHs (1.5 wt.% at 100 bar). These "nanoengineered pores" are defined both by the unique nanostructure self-assembled during synthesis, and by the activated pores during oxidation.

Decoration of SWNHs with Pt and Pd nanoparticles resulted in enhanced binding energy (NREL, 36 kJ/mol), as well as enhancement in the room temperature uptake of 0.6 wt.% (for undecorated, oxidized, pure-C SWNHs at 20 bar), to 1.6 wt% for Pt- and Pd-decorated SWNHs at 100 bar, comparable to MOF-177 materials. NIST neutron scattering on gram quantity Pt- and Pd-decorated SWNHs showed clear evidence for "spillover" type losses of molecular hydrogen and determined the onset temperature for this effect to be between $150K < T < 298K$.High (2142 m^2/g) surface area SWNH materials with variable pore sizes and metal-decorated SWNHs were demonstrated with metals (Pt, Pd) resulting in increased excess storage (3.5 wt. % at 77K). Compression results in bulk SWNH samples with density 1.03 g/cm^3, and 30 g/L volumetric capacity.

Energy calculations were performed to predict the morphology of different metals on C supports, and understand the clustering process which results in non-uniform metal decoration. Modeling in the project predicted that the alkaline earth metals Ca and Sr should have a special ability to coat carbon nanostructures without clustering to form a coating layer exhibiting a region with sufficient electric field strength to polarize and bind H_2 with 8.4 wt. % excess uptake and 0.4 eV binding energy(for Ca).Methods of vapor phase Ca-decoration were then developed and found to result in smooth decoration, in agreement with theoretical predictions. Hydrogen adsorption isotherm measurements were performed at 77K and 0.9 atm to compare the Ca-decorated oxidized SWNHs (o-SWNHs) with the undecorated o-SWNHs. The isotherms were reversible indicating that Ca-decorated, higher surface area nanoporous carbons are promising materials for enhanced hydrogen storage capacities. Metal decoration with Ca has been shown to result in smooth nanoparticle-free coatings and anomalously high storage, in agreement with the proposed mechanism of polarization induced by high local electric fields resulting from the alkaline-earth metal "doping" of C by decoration.

In summary, SWNHs were found to be unique carbon nanomaterials which can be produced continuously at high rates from vaporization of pure carbon. Their inherent pore structure exhibits significant room temperature hydrogen storage in sub-nm pores, and their morphology serves as an excellent metal catalyst support for small (2-3 nm nanoparticles). Pt- and Pd-nanoparticle-decorated SWNHs exhibit clear evidence for metal-assisted hydrogen storage which is activated at T>150 K, permitting additional room-temperature storage up to 1.8 wt.% at 100 bar. One of the key results of the project were theoretical predictions for doped, decorated, and filled nanostructures with distributed charge to maintain high static electric fields sufficient to polarize and bind hydrogen.This concept indicates a promising new direction for hydrogen storage materials.

Project Goals

Overall, the project objectives were to:

- Assess 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.
- Tune the shape and size of the individual nanohorns as well as their interstitial pore sizes in their aggregates by varying their synthesis conditions and by post-processing chemical treatments in order to nano-engineer their pore architecture for optimal hydrogen uptake by maximizing supercritical hydrogen adsorption and metal-catalyzed "spillover".
- Develop the theoretical framework to understand, predict, and guide the experimental approaches to develop metal-decorated SWNHs with high dihydrogen binding energy and excess storage.

Technical Barriers

This project addressed the following technical barriers from 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 developed nanoengineered metal-decorated carbon nanohorns for use as effective hydrogen storage media to satisfy DOE system targets. The project addressed 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 5kg system fill

Summary of Project Accomplishments

Overall, the project met its primary goals and objectives, and reoriented toward a new pathway for tailored, metal-decorated carbon nanostructures, finding that:

- Carbon nanohorns are excellent metal catalyst supports, manufacturable in high rates from economical raw material, and are unique nanomaterials synthesized from the “bottom-up” with well-defined, sub-nm pores.
- The shape and size of the individual nanohorns, as well as their interstitial pore sizes in their aggregates could be varied during synthesis and in post-processing treatments to provide high surface area materials with sub-nm pores that exhibit significant room-temperature storage. In addition, their morphology served as excellent supports for metal catalysts and these decorated materials served as good materials to probe metal-assisted hydrogen storage effects.
- A mechanism of *polarization induced by high local electric fields* was theoretically proposed to result from alkaline-earth metal coating of C surfaces. Experimentally, decoration of SWNHs and AX-21 activated carbon with Ca was shown to result in smooth nanoparticle-free coatings and anomalously high storage, in agreement with these predictions. These results indicate a promising pathway to theoretically predict and experimentally develop nanoarchitectures for hydrogen storage.

Specific Accomplishments

- High surface areas: SWNHs were synthesized in gram quantities with pore sizes adjusted to maximize surface area (2142 m^2/g) and increase excess storage (3.5 wt. % at 77K).
- Volumetric Capacity: Compressed SWNH pellets with 1.03 g/cm3 density were demonstrated, corresponding to volumetric capacities of 30 g/L.
- Tunable, small pores: NMR confirmed the majority of storage in the interstitial (~ 0.5 nm) pores on large SWNHs, and in activated pores (< 1 nm) in short-SWNHs. These NMR shifts are the highest among all materials studied, indicating storage in very small pores. Work continues to understand the activation process, but is aided by the stability of the nanohorn aggregate structure which is defined at very high temperatures during synthesis.
- Room temperature storage: Undecorated, short O-SWNHs reversibly store significant hydrogen (0.6 wt.% at 30 bar) at room temperature, comparable to bridged MOFs and Pt-decorated O-SWNHs (1.5 wt.% at 100 bar). These “nanoengineered pores” are defined both by the unique nanostructure self-assembled during synthesis, and by the activated pores during oxidation.
- Enhanced binding energy:Decoration of SWNHs with Pt and Pd resulted in enhanced binding energy (NREL, 36 kJ/mol), and enhanced room temperature uptake from 0.6 wt.% for

oxidized, pure-C SWNHs at 20 bar, up to 1.5 wt% (100 bar) for Pt-decorated SWNHs comparable to MOF-177 materials.

- Evidence of spillover in metal-decorated SWNHs:Neutron scattering (NIST) on gram-quantity Pt- and Pd-decorated SWNHs showed evidence for “spillover” type losses of molecular hydrogen and determined the onset temperature between 150K < T < 298K.
- Theoretical determination of metal clustering mechanisms and survey of candidate metals for enhanced binding of hydrogen - In a survey of all the elements, alkaline earth metals **Ca and Sr** were shown to have a special ability to coat C nanostructures without clustering. The decorated carbon nanostructures were predicted to exhibit sufficient electric field strength near their surface to polarize and bind H_2 with 8.4 wt. % and 0.4 eV (for Ca). This suggested a new direction for nanoengineered architectures with high surface areas and permanent high electric fields to bind hydrogen through electric-field induced polarization.
- Enhanced Binding Due to Ca Decoration - Metal decoration with Ca resulted in smooth nanoparticle-free coatings and anomalously high storage, in agreement with the proposed mechanism of polarization induced by high local electric fields resulting from the alkaline-earth metal “doping” of C by metal decoration.

Project Narrative

Overview

Single-walled carbon nanohorns (SWNHs) were discovered in 1999 by Sumio Iijima in Japan. SWNHs are carbon nanostructures with a unique morphology for metal catalyst supports, electrodes, and hydrogen sorption. 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 (Fig. 1). They can be functionalized by tailoring their pores and by metal decoration. They 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 was 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.

Approach

Carbon nanohorn aggregates are assembled from the *“bottom up”* fromindividual nanohorns,

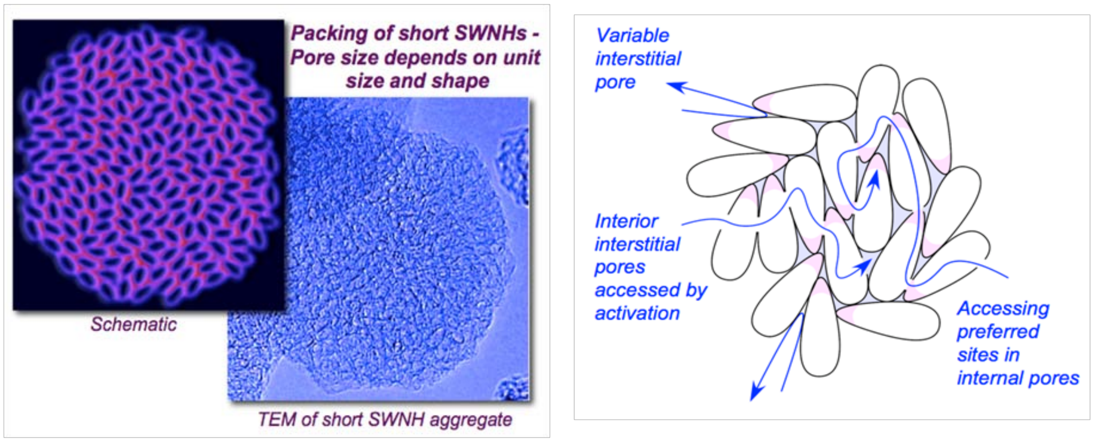

Figure 1. (left) Schematic of a SWNH aggregate, as compared with an actual TEM image. (right) Schematic of the sites for hydrogen storage in a nanohorn aggregate. When each nanohorn subunit is opened by oxidation, the interior pores become accessible, including preferred tip-sites. In addition, the interstitial pores between the nanohorn units are functions of their packing and processing. Slit pores introduced by oxidation provide additional sites for adsorption.

as shown in Fig. 1.

Our project's approach was threefold. First, the shape of individual nanohorns was tuned during synthesis to understand the morphologies with preferred adsorption sites and high binding energies (e.g., in the tips of SWNHs). Second, the nanohorn aggregates have innate interstitial pores which can be tuned by oxidative treatments and other processing techniques (heat, compression, etc.). The internal pores and external pores could therefore be investigated separately. Thus, the nanospaces of the pure carbon framework could be engineered to understand and optimize hydrogen storage in these *"bottom up"* assembled, pure-carbon structures. Third, metals are used to coat or decorate the activated aggregates to explore spillover based storage or store hydrogen directly on the metal coating. This overall approach permits the storage due to engineered nanospaces and that resulting from metals to be explored and tuned separately.

Results

The morphology of the SWNHs was adjusted by tuning the pulse width and energy of the laser used in the carbon vaporization process, producing "large" and "small" carbon nanohorns as shown in Fig. 2 (left).

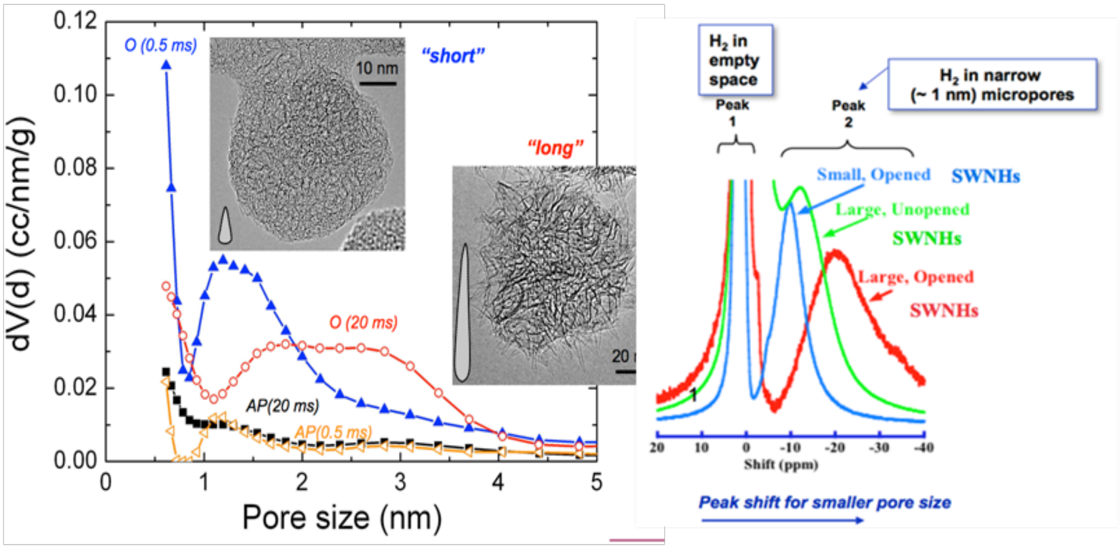

Figure 2. (left) TEM images and corresponding BET pore size distributions for "short" and "long" SWNHs, both "as produced" (AP) and "oxidized" (O). The large interior volumes of the "long" SWNHs were eliminated by tuning the synthesis conditions. (right) NMR measurements reveal that large, opened SWNHs store hydrogen in their interstitial pores, while short-opened SWNHs store the majority of hydrogen in their internal pores.

The pores responsible for the majority of hydrogen storage in these as-produced and activated ('opened') aggregates were measured and compared using a nuclear magnetic resonance (NMR) techniqueby HSCoE partners at the Univ. of North Carolina. The results (Fig. 2, right) revealed that hydrogen storage sites in aggregates of 'large' nanohorns possess are different from those in 'small' SWNHs. 'Large' SWNHs have interstitial pores which store significant quantities of hydrogen in sub-nm pores. 'Small' SWNHs have interstitial pores too small to store significant hydrogen, however the internal and slit pores of the small SWNHs, revealed after oxidation, are the favored sites for hydrogen storage. These results indicate that interstitial pores provide more opportunity as preferred sites for hydrogen storage than previously recognized, and that synthesis conditions should be tuned to optimize the pore volume in these sites. Current modeling efforts are not well suited to calculations of pore sizes and volumes in such aggregates, and this is a promising area for continued experimental and modeling work.

Throughout the project, techniques for pore size measurements were developed within our program and those of the partners with extremely useful diagnostics such as those at the Univ. of North Carolina revealing which pores are responsible for the measured uptake.

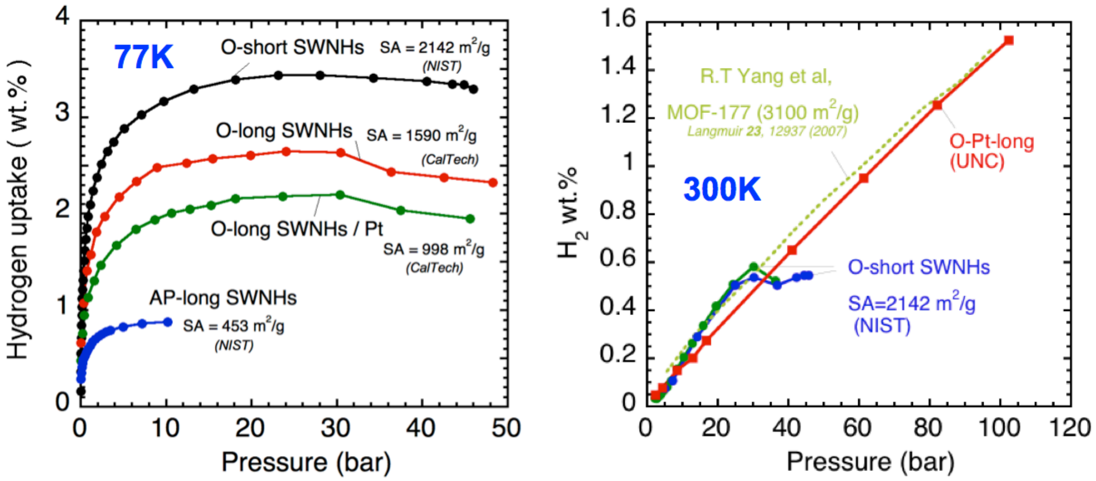

Figure 3. Summary of excess hydrogen uptake at 77K and 300K for oxidized (O) and as-produced (AP) long and short SWNHs, with and without metal decoration (Pt). Measurements by Center partners at NIST, CalTech, and Univ. of North Carolina. Uptake in undecorated SWNHs scale with surface area at 77K, however O-short SWNHs exhibit anomalously high ~0.6 wt.% excess hydrogen uptake at 300K (20 bar). This high storage in O-s-SWNHs saturates, presumably due to limited pore volume. However decoration of O-long-SWNHs with Pt nanoparticles exhibits room temperature uptake extending to 1.6 wt.% at 100 bar, similar to the decorated MOF-177 results from the Univ. of Michigan group of R. Yang.

SWNHs with tunable morphology were synthesized at multigram scale at ORNLand delivered to participants, along with metal-decorated samples. Compared to air oxidation methods used before, new methods of oxidative chemistry using CO_2 to produce same high surface areas (1900 m2/g) with increased pore volumes (from 1.3 ml/g to 1.6 ml/g) and higher yield (from 30% to 70%) were developed. Tuning of pore sizes of SWNHs was demonstrated through oxidation, compression, and thermal treatments.

In order to understand the effects noted for metal catalyst-assisted hydrogen storage, Pt and Pd nanoparticles were controllably deposited onto oxidized SWNHs using wet chemical processing, as shown in Figure 4. High metal loadings were achieved while maintaining high surface areas, and the well-characterized, chemically-processed and decorated SWNHs in gram quantities were delivered to Center partners to probe the spillover mechanism and the enhanced binding energy observed for stored hydrogen. Clear evidence for Pt- and Pd-induced dissociation of molecular hydrogen was observed in Pt- and Pd-O-SWNHs by neutron scattering monitoring of free H_2 by NIST (Fig.4(f)). The onset temperature for catalyst-assisted dihydrogen dissociation and storage was determined to be between $150K < T < 298K$. Nuclear magnetic resonance measurements by As indicated above in Figure 3, NMR measurements at UNC showed 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, *NREL*) and NMR (7.1 kJ/mol, *UNC).* Significant theory and modeling effort was devoted to understand 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.

Our theoretical and computational simulations of metal decoration on carbon supportsrevealedthat charge plays a central role in the clustering behavior of metals on carbon surfaces. Morevoer, charge redistribution of the system was indicated as a mechanism for

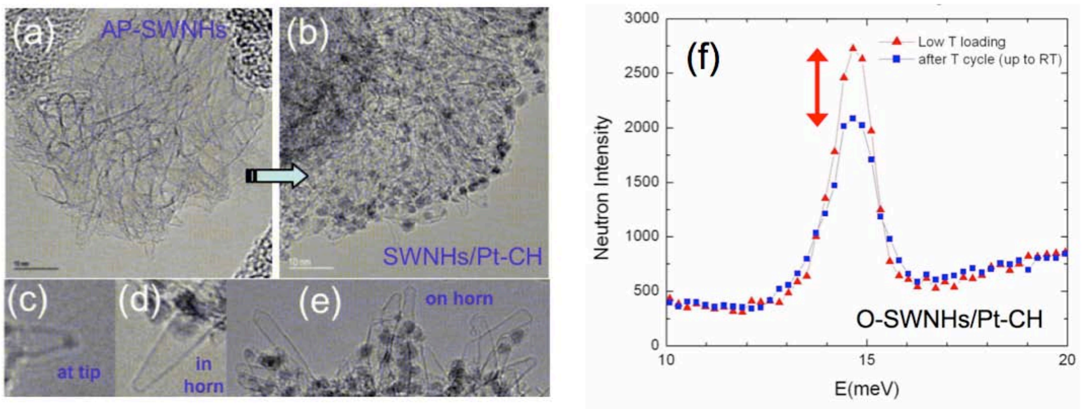

Figure 4. (left) Decoration of as-produced SWNHs in (a) yield Pt-loaded SWNHs shown in (b)-(e) via a wet chemical approach. Similar treatments were performed with Pd. Both Pt- and Pd-decorated O-SWNHs exhibited significant and clear losses in molecular hydrogen at temperatures higher than 150K in neutron scattering experiments performed at NIST (as shown in (f)). Such losses were not observed at lower temperatures, or in undecorated O-SWNHs, providing clear evidence for Pt- and Pd-induced dissociation of molecular hydrogen.

increased hydrogen binding. Our study showed 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 ~0.3eV/H_2) due to polarization of hydrogenmolecules 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 metals to those typically used for decoration of carbon surfaces was performed. The desired material was one which could simultaneously generate strong hydrogen binding sites yet which would be stable against metal clustering. In this way, the entire surface of the carbon support might be used for storage of hydrogen, instead of just in the vicinity of metal nanoparticles, with the lowest weight loading. Of all the elements, alkaline earth metals were found to have the right mixture of charge transfer to the carbon support, and free charge density left to interact with hydrogen.And the lightest of these, 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 Fig. 5indicate that Ca-coated carbon surfaces can bind significant

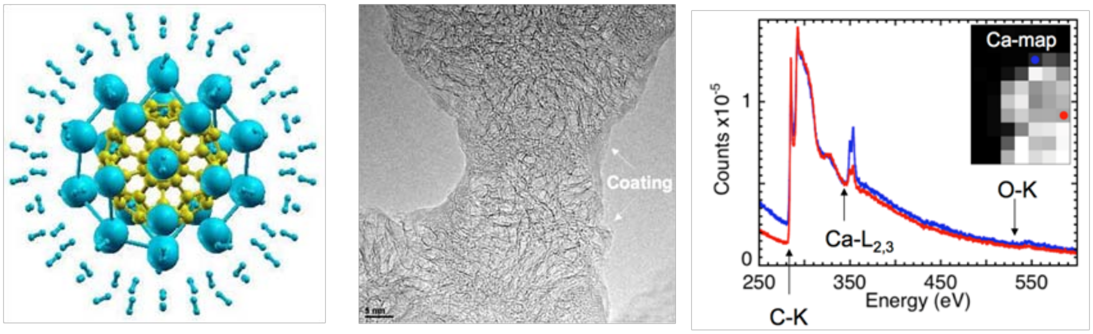

Figure 5. (left) First principles calculations optimization for a Ca-decorated C_{60} surface predicts that Ca will smoothly decorate carbon surfaces, and that the 32 bound Ca atoms will adsorb 92 H_2 molecules which are polarized and bound by the very high electric field which extends past the surface of the (large, blue) Ca atoms, corresponding to a hydrogen uptake of 8.4wt%. (center) Experimentally, smooth Ca-coatings are observed in TEM on SWNH aggregates. (right) EELS mapping confirms the coating on SWNHs and investigates the state of oxidation.

(8.4wt%) hydrogen with withbinding energy ~0.4eV/H_2 suitable for room temperature storage.

Efforts on metal decoration of the activated SWNHs concentrated upon processing techniques to attempt Ca decoration, which is difficult due to the need to maintain oxygen-free conditions throughout the processing, handling, and subsequent testing and characterization.Several processing techniques were implemented to decorate SWNHs with Ca. These included *in situ* vaporization of Ca during SWNH synthesis, vaporization of C into Ca vapor, and post-synthesis infiltration of Ca vapor at high temperatures. The latter technique proved successful. High resolution TEM and Z-contrast STEM/EELS measurements (Fig. 5) were performed to understand whether Ca formed smooth, uniform coatings as predicted by theory. As shown in Figs. 5(b) and 5(c), Ca was uniformly distributed within and on the outer surfaces of opened, small SWNHs. Higher magnification TEM images indicated possible interstitial Ca intercalation in between C layers, as evidenced by interwall spacings of ~0.4nm between the walls of the nanohorns within the aggregates.

Nitrogen surface area measurements of the Ca-coatedSWNHs, however, indicated that the Ca coating resulted in a major reduction in surface area (from ~1200 m^2/g to ~ 300 m^2/g) as shown in Fig. 4. Since the infiltration process did not have *in situ* process control during these experiments, significant coating and pore blocking could be expected. Hydrogen adsorption isotherm measurements were performed at 77K and 0.9 atm to compare the Ca-decorated o-SWNHs with the undecorated o-SWNHs. The isotherms were reversible, and the Ca-decorated o-SWNHs isotherms indicated possible capillary condensation. To account for the difference in surface areas between the different samples, a figure of merit (FOM) was defined as the wt.% hydrogen measured per atmosphere hydrogen gas divided by 500m^2/g. Typically at high pressures, high surface area activated carbons often exhibit 1 wt.% excess adsorption at 77K for every 500 m^2/g surface area (line in Fig. 4, usually obtained at pressures > 20 bar). However it is evident that the Ca-decorated o-SWNHs outperform undecorated samples and exceed this metric even at low (~1 bar) pressures, with a FOM a factor of 4 higher.

In the final stage of the project, based partly upon the prevailing inclination of the newly-formed Manufacturing Center to concentrate upon commercial activated carbons, the same Ca coating techniques were performed upon activated carbons (i.e., AX-21 or MSC-30 obtained fromCalTech). Measurements at ORNL at 1 bar showed a doubling of the room temperature uptake in one of the five Ca-coated MSC-30 samples produced by this technique (Fig. 6). Higher

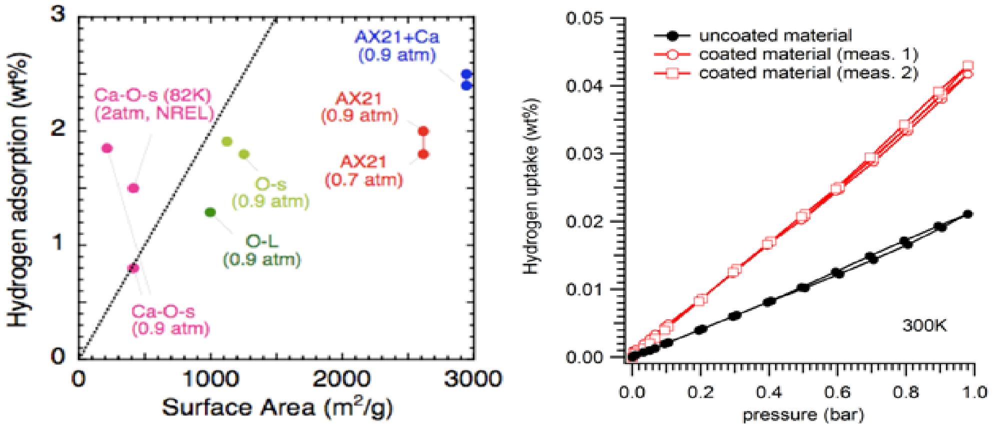

Figure 6. (left) Excess hydrogen adsorption for Ca-coated and uncoated oxidized long (O-L) and short (O-s) SWNHs, as well as AX-21 activated carbon, at 77K. The line indicates a figure of merit of 1 wt.% per 500 m^2/g surface area. Ca-coated SWNHs, despite their lowered BET surface areas, exceeded this figure of merit by as much as a figure of 4. (right) Highly-reproducible best finding for one batch of Ca-coated MSC-30 activated C, where the 3300 m2/g surface area was preserved, and the room temperature storage was doubled in the 0-1 bar hydrogen pressure range compared to uncoated MSC-30. This result was not repeated in 4 subsequent attempts, however the effect within this one batch was highly reproducible (in 5 different samples and multiple runs).

pressure measurements of this sample were contaminated by oxygen during shipment to a partner institution in the Center. As shown in Figure 6, this significant room temperature uptake enhancement in MSC-30 was highly reproducible in multiple samples within this batch, however this effect was not repeated in four subsequent coating runs. High-resolution TEM analysis, EDX analysis, and EELS were able to observe uniformly-decorated calcium throughout the coated activated carbons, but were unable to distinguish what characteristic of the high-storage Ca:MSC-30 was responsible for the doubled room-temperature adsorption. The program was ended before the answer could be obtained, however scalable technologies for more uniform Ca decoration were developed within the program, and it is likely that more uniform annealing (to control oxygen content and functional groups of the MSC-30) in combination with uniform coating technology could repeat the exciting results obtained on this commercially-available carbon.

Conclusions and Future Directions

This program showed that carbon nanohorns are a interesting nanoscale carbon material which can be produced without metal catalysts in high yields and rates. Commercial scale-up of nanohorn production has been demonstrated in the U.S. and is a focus in Italy currently. This material is highly interesting because it forms aggregates with a skeletal structure of internal pores and interstitial pores which are controllable. The project demonstrated that pore sizes in pure carbon nanohorn aggregates can be tuned 1) during synthesis, and 2) during activation, and that this sometimes results in room temperature binding of up to 0.6 wt.% hydrogen at only 20 bar. These values were among the highest in the Center, and show that preferred sites with enhanced binding energies can exist in pure carbon materials.

The SWNHs were used to support the Center's efforts to understand storage due to spillover from Pt- and Pd-metal decoration. SWNHs were produced in gram-sized samples, and then Pt- and Pd-decorated for studies by the Center partners. Pt- and Pd-decorated SWNHswere demonstrated to enhance the storage of SWNHs by an activate process similar to that observed for spillover. Enhanced storage (up to 1.8 wt.%) at room temperature in Pt- and Pd-decorated SWNHs were observed in NMR studies. Importantly, a significant loss of molecular hydrogen at T > 150K was observed by neutron scatteringconsistent with dihydrogen dissociation and storage (i.e. spillover).

However, while efforts in the Center concentrated on theoretically understanding and reliably reproduce experimentally interesting observations of spillover storage, an alternate approach was also being pursued to store hydrogen on the metals which decorated the carbons, i.e. using the carbons as a high surface-area support for thin metal coatings. In our program, computational and theoretical studies of metal decoration processes on carbon surfaces showed the energetic pathways which inevitably lead to nanoparticle formation, and failure to meet DOE targets. A computational and theoretical search was performed for metals which could smoothly-coat, and then store hydrogen in sufficient quantities to meet DOE targets, resulting in the prediction that Ca is the optimal material for this purpose.

A key finding of the project is the hydrogen storage mechanism (*polarization induced by high local electric fields)*at play in hydrogen storage by Ca-decorated carbon. The alkaline-earth metal “doping” of C results in charge transfer between the Ca and C, producing the smooth coating and good binding. However, sufficient charge is left to produce a very high electric field just outside the Ca:C surface that is sufficient to polarize and bind molecular hydrogen. Our experimental studies verified that decoration of both SWNHs and activated carbons result in smooth nanoparticle-free coatings and anomalously high storage in several cases, in agreement with our proposed mechanism.

Future work should pursue this highly promising new direction on two fronts. First, work should continue with high-surface area carbons to maintain high surface areas while uniformly coating these materials. For nanohorns the Ca-coating process can be optimized by integrating it as an inherent part of the synthesis process, while for activated carbons *in situ* process monitoring during infiltration should be implemented. Second, new materials, such as layered organic crystals (e.g., TCNQ salts) or thin films - with built-in high electric fields and nanoengineered spaces sufficient for hydrogen molecules - should be investigated to capitalize on the same principle employed for the nanohorns.

Publications/Presentations

"Theoretical design of nanoscaled energy materials for hydrogen storage", M. Yoon, invited seminar talk at Yonsei University, Seoul, Korea, October 04, 2010.

"Basic energy research on organic molecular crystals", M. Yoon, Y. Miyamoto, and M. Scheffler, contributed talk of at the Psi-k conference, Berlin, Germany, September 12-16, 2010.

"First-principles theoretical studies of hydrogen interaction with ultrathin Mg and Mg-based alloy films", M. Yoon, H.H. Weitering, and Z. Zhang, *Phys. Rev. B* ***83****, 045413 (2011).*

"High-capacity hydrogen storage in metal-free organic molecular crystals" M. Yoon and M. Scheffler *(submitted to Phys. Rev. Lett.).*

"Enhanced dipole moments in photo-excited TTF-TCNQ dimmers" M. Yoon, Y. Miyamoto, and M. Scheffler *(to be published.).*

*"Single-Walled Carbon Nanohorns for Hydrogen Storage and Metal Catalyst Supports",*David B. Geohegan, Invited Presentation at Solid Storage of Hydrogen (SSH-IP) Workshop, Fodele, Greece, June 10, 2009.

"First principles design of electric-field-assisted high capacity hydrogen storage media", M. Yoon, Invited talk at American Physical Society March Meeting, Pittsburgh, Pennsylvania, March 16, 2009.

"Hydrogen storage in charge compensated organic molecular crystals", M. Yoon and M. Scheffler, Contributed talk at American Physical Society March Meeting, Pittsburgh,Pennsylvania, March 18, 2009.

"Hydrogen storage in charge compensated organic molecular crystals", M. Yoon and M. Scheffler, Poster presentation at DPG (Deutsche Physikalische Gesellschaft), Rogensberg, Germany, March 23-27, 2009.

"Electric Field Assisted Hydrogen Storage", M. Yoon, Invited talk at the Workshop on "Hydrogen Storage in Metal-Organic Frameworks", Bremen, Germany, May 6-9, 2009.

"Interaction between hydrogen molecules and metallofullerenes", M. Yoon, S. Yang, Z. Zhang, *J. Chem. Phys.* **131**, 064707 (2009).

"Light Alkaline-Earth-Metal Coated Carbon Fullerenes as Effective Hydrogen Storage Media", M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang, Contributed talk at Material Research Society Spring Meeting, San Francisco, CA, March 26, 2008.

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Acronyms

TEM: transmission electron microscopy

SEM: scanning electron microscopy

TGA: thermal gravimetric analysis

BET: Brunauer, Emmett, and Teller surface area measurement

TPD: temperature programmed desorption

NMR: nuclear magnetic resonance

EDX: energy dispersive X-ray

SWNH: Single-walled carbon nanohorn

Z-STEM: Z-Contrast scanning transmission electron microscopy

EELS: Electron energy loss spectroscopy