

IV.C.1c Theoretical Models of H₂-Carbon Systems for Hydrogen Storage and Optimization of SWNT

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Objectives

- Model materials structures' interaction with hydrogen, optimize their makeup for storage, and assess the gravimetric and volumetric capacity. Provide recommendations for the synthetic goals (e.g. pore/channel size, metal enhancement routes, spillover receptors).
- Explore full utilization of physisorption by van der Waals forces through carrier geometries—3D-foams for best surface, accessibility, and retention capacity-binding energy. Compute van der Waals wells for H₂-trapping on generic carbon structures, for achieving 7-9% storage.
- Explore transition-metal enhanced adsorption via the various ways of doping carbon backbone Me@Cn + m*H₂, Me = Sc, Ti, ... or Li, K, with the emphasis on metal aggregation.
- Investigate synthesis of metal- and electronegative-group- (F, BF₃) enhanced vertically aligned nanotube arrays (VANTA) (in contrast to fibers) for H₂ adsorption.
- Develop theory of hydrogen spillover, its thermodynamics, and kinetics, including energy states, cooperative effects, and mobility.

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
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project involves conducting fundamental studies of carbon-based 3D-structures (including metal enhanced structures) for physical and chemisorption of hydrogen. Insights gained from these studies will be applied towards the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Gravimetric content, up to 7%
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Identified a kinetic path to the cross-welding of nanotubes (or VANTA material), which shows how the nano-foams can be engineered via physical processing. The foam has nanometer pores and channels; all its surface (~2,600 m²/g) is all-accessible; it's lighter than water (~0.9 g/cm³); is an excellent thermal conductor (favorable for thermal management); and it is metallic.
- Defined best growth parameters for an atomic hydrogen activated rapid insertion reactor; growth rate ~2 μm/min; VANTA as thick as 1 mm. Nanotube (NT) non-fiber scaffolds are now available (to the National Renewable Energy Laboratory [NREL] and Air Products and Chemicals, Inc. [APCI]) for 3-D engineering and addition of metals or electronegative- (F, BF₃) enhancers for H₂ adsorption.
- Performed extensive computational studies of thermodynamics of spillover, that is, of specific H-bound configurations as compared to the energy of molecular H₂. Specific clusters are proven favorable, stable, and diffusion must display localized front behavior.



Introduction

The search for novel materials capable of efficiently storing hydrogen for on-board energy use needs guidance from modern materials science, which includes predictive theoretical tools. In this project we combine accurate theoretical models with small-scale pilot synthetic efforts; this activity allows us to provide material design suggestions to the Hydrogen Sorption Center of Excellence (HSCoE) partners, while also verifying selected experimental approaches in-house. Work done in this project allows DOE to see more promising paths to meeting its goals (e.g. 3D-architectures with optimum spacing and metal-enhancement), while down-selecting some others which computational analyses do not support as feasible (e.g. densely packed raw single wall nanotube [SWNT] material).

Approach

The modeling approach combines quantum-chemical *ab initio* and, wherever possible, classical force field potentials to achieve the accurate yet affordable predictive description of nano-structured systems storage, with sufficient flexibility to add analysis of the systems that emerge within the Center as promising storage candidates. The synthesis approach utilizes novel VANTA growth methods and advances its flexibility towards developing materials best suited for H-storage.

Results

For a previously proposed concept of 3D-structures (cross-linked or foams) we made progress in identifying best geometry for storage. For example, the simple array of covalently linked carbon tubes appears to be better with mono- than with double *p*-phenylene cross links (Figure 1a). For the foams, we have identified a kinetic path to the cross-welding of nanotubes (or VANTA material), which shows how the nano-foams can be engineered via physical processing. The foam has nanometer pores and channels with all of its surface ($\sim 2,600 \text{ m}^2/\text{g}$) accessible; it is lighter than water ($\sim 0.9 \text{ g/cm}^3$), has excellent thermal conductivity advantages, and is metallic. Furthermore, we have computed the binding energy landscape within the foam (Figure 1b).

We have performed precise H-C frequency computations, in order to determine the expected signature for different hydrogen binding positions (Figure 2) and to help our partners at the National Institute for Standards and Technology (NIST) to recognize the features in their planned neutron-scattering experiments.

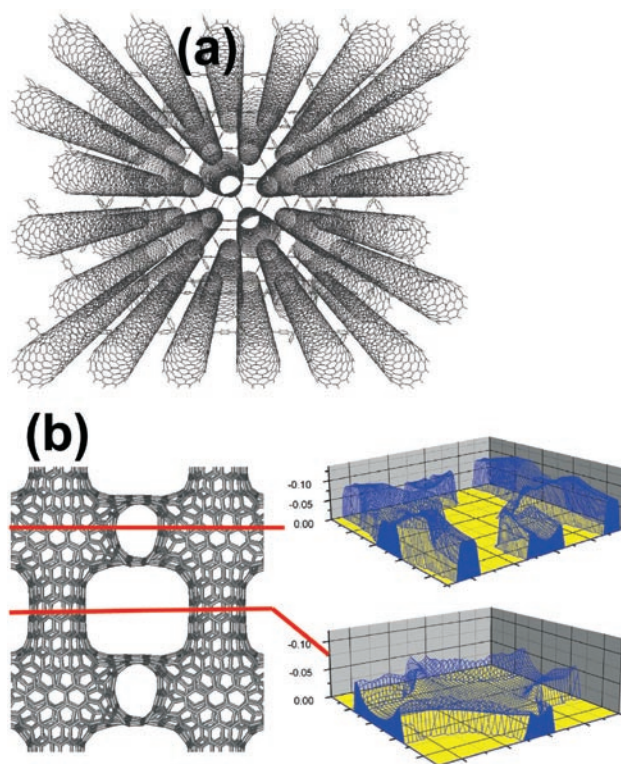


FIGURE 1. (a) SWNT Bundle Functionalized with *p*-Phenylene (The neighboring tubes in the bundle are separated by a benzene functional group and the vdW gap is kept at 0.67 nm.) (b) The Absorption Energy Landscape within the Open-Pore Welded 3D-Foam

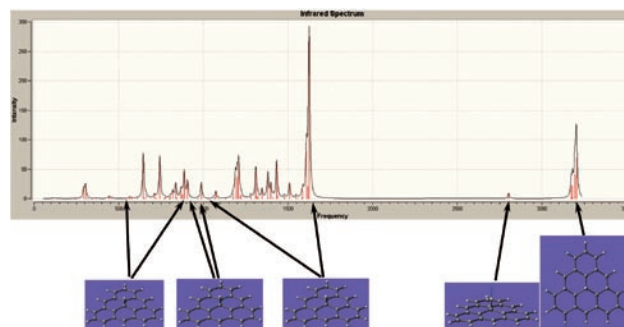


FIGURE 2. Calculated Frequencies of the Chemically Adsorbed Hydrogen Atom on Graphene, to be Compared with Experimental Measurements (at NIST)

In the synthetic effort, VANTA scaffolds have been produced (Figure 3). The best growth parameters have been defined for an atomic hydrogen activated rapid insertion reactor, with a growth rate $\sim 2 \mu\text{m}/\text{min}$ and VANTA as thick as 1 mm. NT non-fiber scaffolds are now available for 3-D engineering and addition of metals or electronegative- (F , BF_3) enhancers for H_2 adsorption (in collaboration with NREL and APCI).

We have performed extensive computational studies of spillover thermodynamics with a number of H-bound

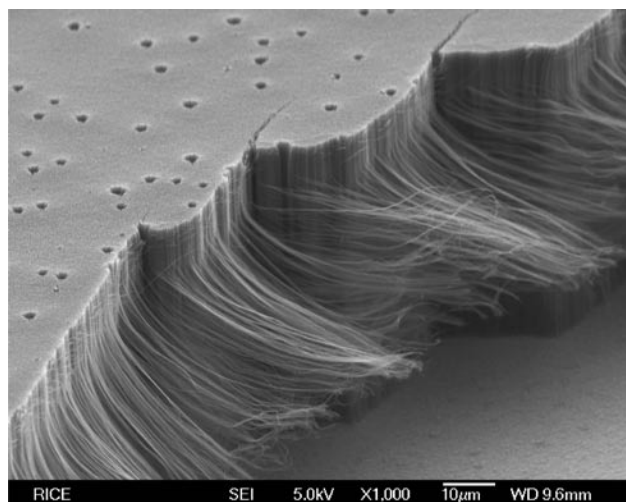


FIGURE 3. Example of High Resolution Image of VANTA Sample Produced at Rice (R. Hauge, Unpublished)

configurations, as compared to the energy of free molecular H_2 (Figure 4). Importantly, we discovered that specific clusters are favorable: stable and with diffusion that displays localized front behavior. These are important findings as they provide the atomistic view basis for understanding spillover and further study of its kinetics.

Future Directions

- Evaluate SWNT-based 3D-foam capacity by direct Monte-Carlo simulations. Further refine van der Waals force-field, with an eye on topological and elastic curvature effects. Develop statistical-thermodynamics model for H_2 “pumping” into potential wells provided by carbon-based carrier material.
- Compute detailed binding strength and mobility barrier for metal-centers. Determine stable sites which prevent aggregation of Me. Determine size of Me-cluster where Kubas’ interactions transition into the dissociative (and spillover commences).
- Densify VANTA for H_2 adsorption testing. Perform Li-decoration, functionalization with fluorine and BF_3 in order to create highly charged nanotube salts, and test for H_2 adsorption.
- Perform precise energy calculations of:
 - H@receptor configurations (along with v-signatures for experimental detection);
 - other receptor geometry/materials, e.g., metal organic frameworks, Met-Car;
 - dynamics of the chemically bound/absorbed hydrogen atoms including barriers and sigmatropic selection rules for H-hopping; and

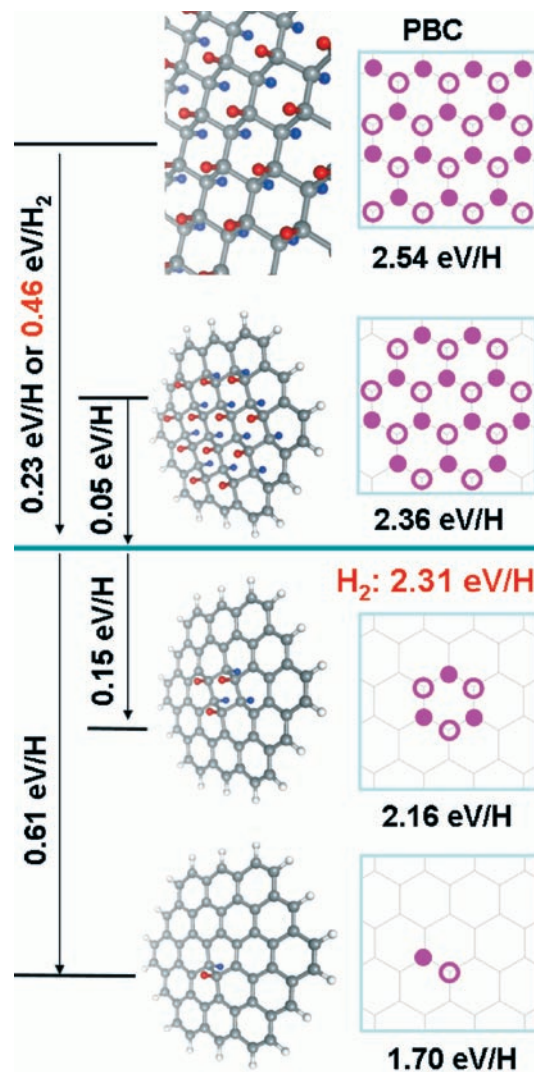


FIGURE 4. Average Binding Energy of the Chemically Absorbed Hydrogen Atom Blocks (size of 2, 6, 24, ∞ of Hydrogen Atoms) on Graphene, Compared to the Cohesive Energy of Free Hydrogen Molecule, H_2

- diffusion of H atom from catalyst to graphene and the rate of spread, using quantitative front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion.

FY 2007 Publications/Presentations

1. “Topological Defects Dependence of Hydrogen Absorption on Graphene Layer: Comparison of Physical and Chemical Adsorption,” F. Ding, P. Krasnov, B. I. Yakobson, in preparation.
2. “Designing Carbon Nanoframeworks Tailored for Hydrogen Storage,” P.F. Weck, E. Kim, N. Balakrishnan, H. Cheng, and B.I. Yakobson, *Chem. Phys. Lett.*, **439** (2007) 354-359.

3. “Calculating Carbon Nanotube–Catalyst Adhesion Strengths,” P. Larsson, J.A. Larsson, R. Ahuja, F. Ding, B.I. Yakobson, H. Duan, A. Rosén, and K. Bolton, *Phys. Rev. B*, **75**, 115419 (2007).
4. “Meta-Foams from Carbon Nanotubes for Hydrogen Storage,” F. Ding, Y. Lin, P. Krasnov, B. I. Yakobson, submitted (2007).
5. “Aggregation of Light Transition Metal Atoms on Carbon Nanotubes and Effect on the Hydrogen Storage,” P. Krasnov, F. Ding, and B. I. Yakobson, in preparation.
6. “Fullerene Cage Capacity for Hydrogen Storage,” O.V. Pupyshcheva, A.A. Farajian, and B.I. Yakobson, *Chem. Phys. Lett.*, submitted (2007).
7. “Continued Growth of Single-Walled Carbon Nanotubes,” Wang, Y. H.; Kim, M. J.; Shan, H. W.; Kittrell, C.; Fan, H.; Ericson, L. M.; Hwang, W. F.; Arepalli, S.; Hauge, R. H.; Smalley, R. E., *Nano Letters* 2005, **5** (6), 997-1002.
8. “Functionalization and Extraction of Large Fullerenes and Carbon-Coated Metal Formed During the Synthesis of Single Wall Carbon Nanotubes by Laser Oven, Direct Current Arc, and High-Pressure Carbon Monoxide Production Methods,” A. K. Sadana, F. Liang, B. Brinson, S. Arepalli, S. Farhat, R. H. Hauge, R. E. Smalley, and W. E. Billups, *Journal of Physical Chemistry B*, **109** (2005) 4416.
9. Electrochemical Society Meeting, May 2007, Chicago, IL, presentation (delivered by B. I. Yakobson).
10. FreedomCar Technical Team meeting, February 2007, Golden, CO, presentation (delivered by B. I. Yakobson).
11. FY 2007 Merit Review, May 2007. Crystal City, VA (oral presentation).