

## IV.C.1i Optimization of Nano-Carbon Materials for Hydrogen Sorption

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### Objectives

- Overall: model materials structures' interaction with hydrogen, optimize their makeup for storage and assess the volumetric and gravimetric capacity. Provide recommendations for the synthetic goals, e.g. pore/channel size, metal enhancement routes.
- Identify obstacles (thermodynamics and kinetics) for the spillover, e.g. metal aggregation, and develop conceptual model of the process for its improvement.
- Estimate the volumetric and the gravimetric capacities of the 3-dimensional (3D) foam and compare with the carbon nanotube (CNT)-bundles.
- Quantify and optimize the volume and weight percentage of hydrogen physisorbed onto high surface area carbon-based superacids.

### 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

### Technical Targets

Develop carbon-based 3D-structures (including metal enhanced structures) for physical and chemisorption of hydrogen. Apply the gained insights 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

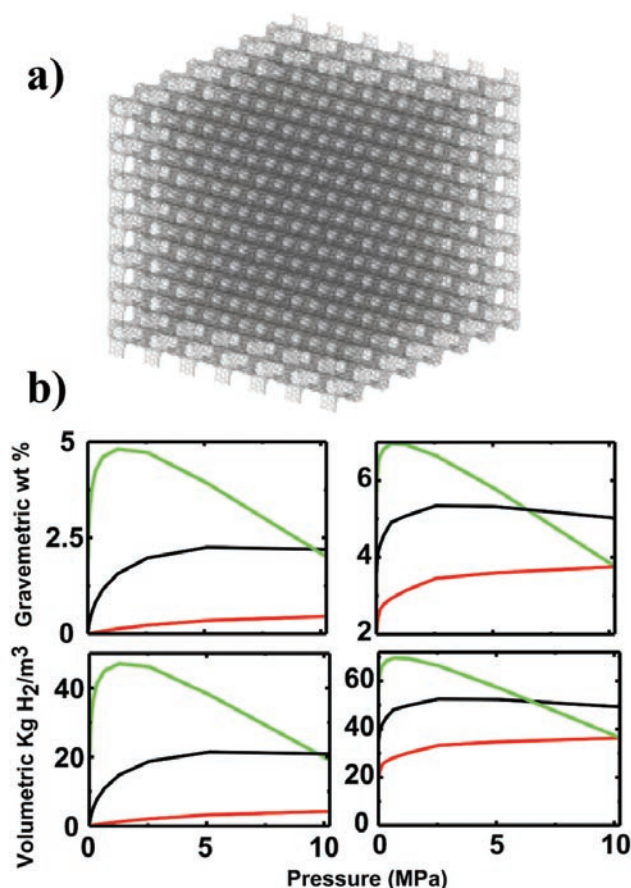
### Accomplishments

- Carried out Grand Canonical Monte Carlo (GCMC) simulations to determine the storage capacity of previously designed 3D-foam. The gravimetric and volumetric capacities of foams are found to surpass the well-separated, equivalent diameter nanotube bundles. At 77 K the storage capacities (up to 7%, Figure 1) are close to metal organic framework (MOF) and could meet the DOE goal.
- Developed first thermodynamically consistent model of spillover-chemisorption of hydrogen as a nucleation of a new phase on graphene (binding energy of  $\sim 0.23$  eV/H), with 7.7% gravimetric.
- Addressed the overall thermodynamics of the spillover, on a free and supported metal cluster. Although it is difficult, thermodynamically, to achieve spillover on a pristine graphene, we demonstrate that the presence of phase nucleus of hydrogenated graphene makes the process dramatically more favorable.
- Designed and constructed direct elemental fluorination reactor with the ability to add another gas such as boron trifluoride and other strong Lewis acids. Samples can be created and handled without exposure to air.



### 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 synthesis efforts; this activity allows us to provide material design suggestions to the Hydrogen Sorption Center of Excellence partners, while also to verify selected experimental approaches in-house. Work done in this project allows the Center to see more promising



**FIGURE 1.** a) The structure of the 3D nano-foam. b) The gravimetric and volumetric % of H<sub>2</sub> in the nano-foam by GCMC. The left and right plots are obtained using weak [2] and strong [3] C-H<sub>2</sub> potentials, at T = 77 K (green), 150 K (black) and 298 K (red).

paths to meeting its goals (e.g., 3D-architectures with optimum spacing or enhancement of spillover by introduction of heterogeneous nucleation via bridges), 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 predictions of nano-structured systems. GCMC simulations are used, with the judicious choice of interaction potentials, to estimate the storage capacities under ambient conditions. The synthesis approach utilizes novel vertically aligned nanotube arrays (VANTA) growth methods and advances its flexibility towards developing materials best suited for H-storage.

## Results

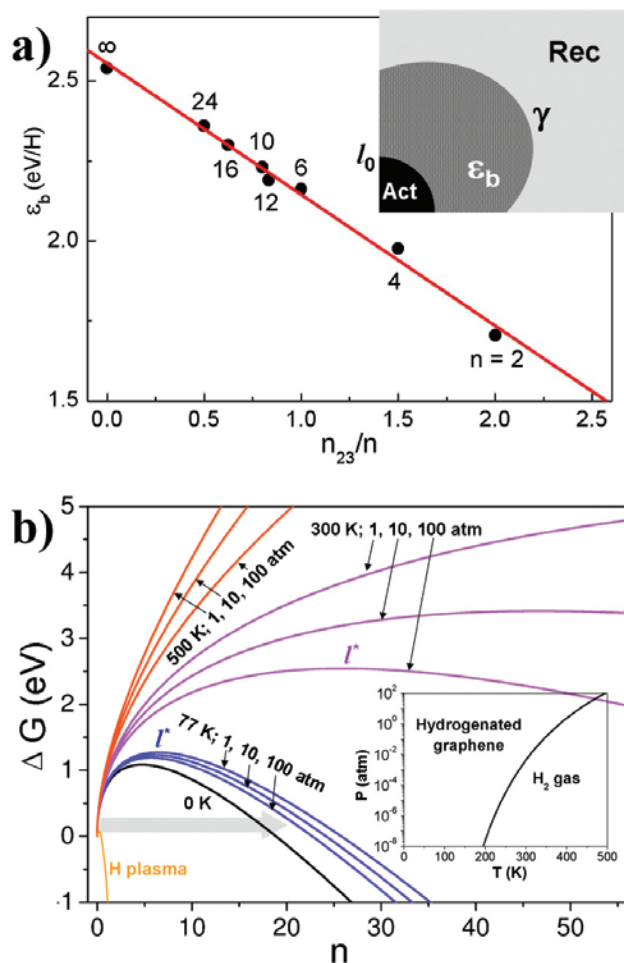
We have computed the foam's storage capacity by performing GCMC simulations at finite temperature and pressure. The excess capacity is shown in Figure 1b (up to 7% gravimetric at 77 K) and is larger than for the well-separated nanotubes bundle, while comparable to the capacities of MOF, and meets the DOE target of wt and vol%. The ease of synthesis (e.g. via using zeolites as templates) of nano-foams makes them a promising material.

Achieved understanding of thermodynamics of hydrogen gas spillover into the chemisorbed state on graphene. In the latter, H atoms tend to group into compact clusters; influenced by aromaticity rules and the pyramidalization strain compensation, so that the "magic" (lowest energy) clusters consist of closed six-hydrogen rings. Computed Gibbs formation energy  $\Delta G_{P,T}(n)$  plots (Figure 2) display typical phase nucleation dependencies, with the nucleus barrier  $\Delta G^*$  and the corresponding critical size  $n^*$  (or  $l^*$ ) identified for arbitrary pressure and temperature conditions. Important applied aspect of this analysis is that the balance between the fluidic gas phase and the immobilized "7.7 wt% storage-phase" can be changed in either direction by changing pressure and temperature not too far from the ambient conditions, thus permitting in principle reasonable refueling cycles.

We explored the issue of metal clustering in the Me-decorated carbon-based materials for storage. It appears energetically and kinetically possible at room temperature. The key in achieving the theoretical limit of storage capacity in such system is to pin the metal atoms by using dopants or defects, as shown at the National Renewable Energy Laboratory (NREL) with the boron doping [1].

We further studied the activity of metal catalyst, as important constituent of spillover process, by calculating the binding energies of H<sub>2</sub> on a free as well as graphene-supported Pd<sub>4</sub>. These energies serve as chemical potential for H, and determine the onset of the spillover. We compute the migration barriers (0.68 eV, kinetically feasible at practical temperatures) for the motion of H from metal cluster to the H-graphene phase, Figure 3. Our results show that the presence of hydrogenated phase of graphene makes the spillover step from metal to receptor thermodynamically favorable.

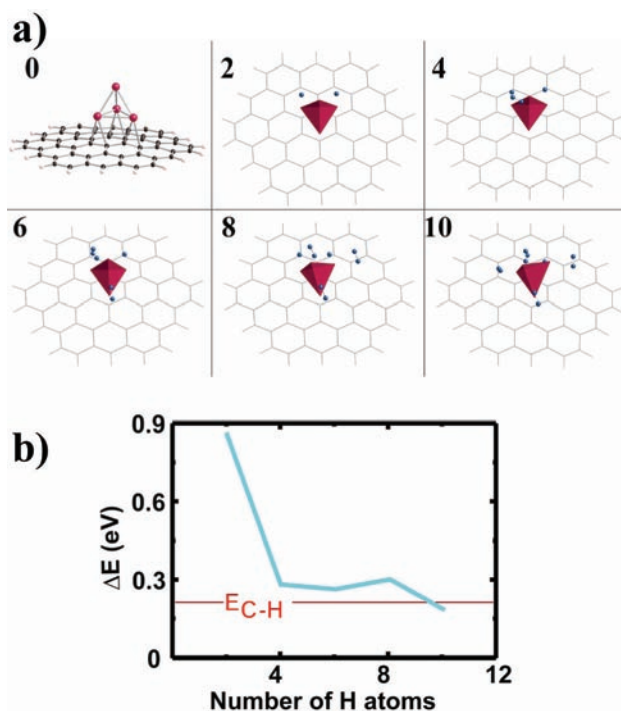
Parameters for best growth of VANTA scaffolds have been defined and VANTA are now available for addition of electronegative groups for enhanced H<sub>2</sub> adsorption. A variable temperature reactor has been built and tested for controlled exposure of samples to fluorine and boron trifluoride. One gram samples have been converted to a carbon nanotube salt, to be tested for H uptake by NREL and Air Products.



**FIGURE 2.** a) The computed binding into compact aromatic clusters depends linearly on the portion  $n_{23}/n$  of  $sp^2$ - $sp^3$  bonds. b) Gibbs free energy of formation of a CH-island in the graphene as a function of number of H atoms, computed for different pressure and temperature. Typical nucleation-type shapes are characterized by the critical nucleus size (number of atoms  $n^*$  or dimension  $l^*$ ).

## Conclusions and Future Directions

- Storage capacity of 3D-foam assessed and found to surpass the CNT bundles (comparable to MOF).
- Catalytic activity of metal clusters in spillover was investigated and the onset of spillover on the receptor was computed.
- Hydrogenated phase nucleus and the Me-cluster saturation are the key elements for spillover.
- Reactor is constructed for conversion of carbon systems to superacid salts, VANTA have been converted to superacid salts.
- Future spillover thermodynamics work: effects of metal cluster size, dopants, bridges, on the H migration from activator to receptor (along with v-signatures for experimental detection). Extend to other receptor geometry/materials (MOF, Met-Car).



**FIGURE 3.** a) The optimized structure of  $Pd_n@graphene$  ( $n = 0$  to  $10$ ). b) The plot of incremental energy  $E_{incr}$  versus number of H atoms. The red line shows the H binding energy in fully hydrogenated phase. The  $E_{incr}$  crosses this line after 5<sup>th</sup> H atom, indicating the thermodynamic onset of spillover.

- Explore the mobility of the metal cluster for possible “scooter” effect, when the adsorbed H does not move, rather the metal moves.
- Generate array of the 3D-foams for optimal storage capacity. Evaluate experimentally accessible surface areas using GCMC. Develop code for generating isotherms “on the fly” for arbitrary C-based structures. Consider storage-enhancing doping of the 3D-foams.
- VANTA and high surface area carbon superacid salts will be optimized for H<sub>2</sub> storage. Other  $\pi$ -delocalized carbon systems such as giant fullerenes and graphene sheets will be converted to superacid salts and tested for storage. Nitrogen-doped carbon systems will be made for conversion into superacid salts.

## Special Recognitions & Awards/Patents Issued

1. Our work published in Nano Letters was selected as Cover article (March 2008).
2. DOE Hydrogen Program R&D Award (June 2008).
3. B.I.Y. received 2008 Nanotech Briefs Nano 50 Innovator Award (July 2008).

## FY 2008 Publications/Presentations

### Publications

1. “Designing carbon nanoframeworks tailored for hydrogen storage”, P.F. Weck, E. Kim, N. Balakrishnan, H. Cheng, and B.I. Yakobson, *Chem. Phys. Lett.*, **439**, 354-359 (2007).
2. “Nanotube derived carbon foam for hydrogen storage”, F. Ding, Y. Lin, P. Krasnov, and B.I. Yakobson, *J. Chem. Phys.*, **127**, 164703 (2007).
3. “Clustering of Sc on SWNT and reduction of hydrogen uptake: ab initio all-electron calculations”, P.O. Krasnov, F. Ding, A.K. Singh, and B.I. Yakobson, *J. Phys. Chem. C, Letters*, **111**, 17977-17980 (2007).
4. “Hydrogen storage on graphene as a phase nucleation process”, F. Ding, Y. Lin, B.I. Yakobson, *Phys. Rev. B* **78**, 041402-R (2008).
5. “Fullerene nanocage capacity for hydrogen storage”, O.V. Pupyshcheva, A.A. Farajian, and B.I. Yakobson, *Nano Letters*, **8**, 767 (2008).

### Presentations

1. “Spillover mechanism for hydrogen storage”, B.I. Yakobson, DOE Theory Focus Session on Hydrogen Storage Materials, April 24, 2008, San Francisco.
2. “Hydrogen storage in carbon based materials physical, Kubas, and chemical adsorption, Feng Ding, Pavel O. Krasnov, Yu Lin, Abhishek Singh, Boris I. Yakobson, MRS Spring Meeting, San Francisco, March 24-28, 2008.

3. “Metal clustering and catalytic spillover on the nanotubes and graphene for hydrogen storage”, Feng Ding, Yu Lin, Abhishek Singh, Boris I. Yakobson, APS March Meeting, New Orleans, March 10-14, 2008.
4. Lecture at the Fundamentals and Applications of Nanotechnology Lockheed-Martin Corporation Workshop, October 11, 2007.
5. “Can superplasticity of 2D lattice help nanostructure engineering for H storage”, Boris I. Yakobson, CMSM Coordination Meeting in Ames, Iowa, Oct 5-6, 2007.
6. “Carbon nanostructures and energy storage”, Department of Materials Science and Engineering, Cornell University, Ithaca, New York, April 26, 2007.

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1. Y. Zhao *et al.*, *Phys. Rev. Letts.* **94**, 155504 (2005).
2. S.C. Wang *et al.*, *J Low Temp Phys* **41**, 611 (1980).
3. S. Patchkovski *et al.*, *PNAS* **102**, 10439 (2005).