

## IV.C.1j Optimization of SWNT Production and Theoretical Models of H<sub>2</sub>-SWNT Systems for Hydrogen Storage

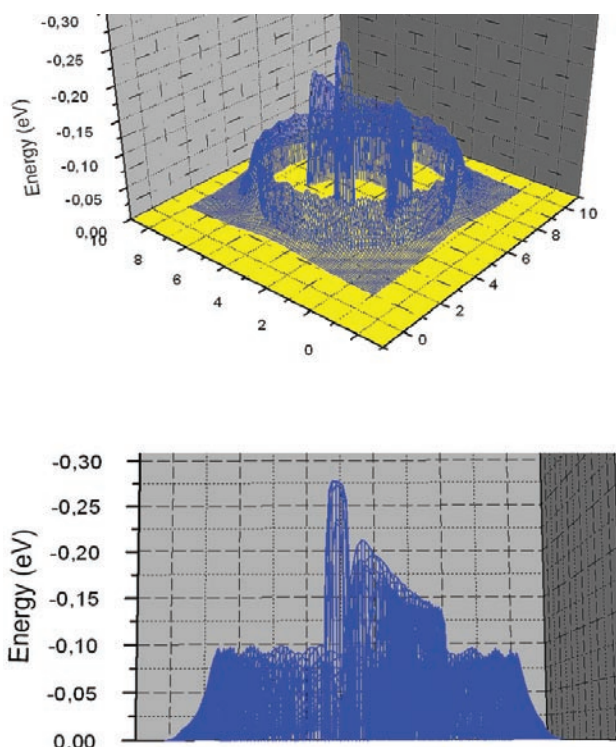
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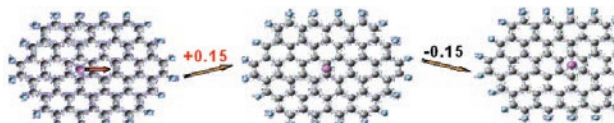
**FIGURE 1.** Example of a computed map of the binding energy for a H<sub>2</sub>-molecule in the proximity of two off-centered nanotubes shows variability of the potential.

### Partner Approach

Rice is developing advanced hydrogen sorption materials by (1) improving the capabilities of our high-pressure carbon monoxide (HiPco) synthesis method for making large quantities of SWNTs and (2) combining quantum-chemical *ab initio* and, wherever possible, classical force field potentials to achieve the accurate yet affordable predictive description of nano-structured hydrogen storage systems, with sufficient flexibility to add analysis of the systems that can emerge later as promising storage candidates.

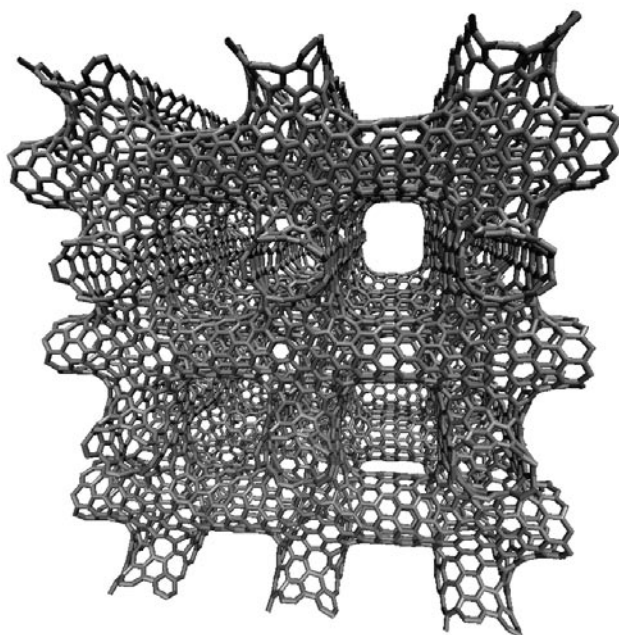
### Partner FY 2006 Results

- Determined parameters for classical empirical Lennard-Jones H<sub>2</sub>-carbon interaction. With this, we performed the necessary “rapid prototyping” of nano-system capacities that are used to compute a map of binding potentials within carbon cages of various geometries (example, Figure 1).
- Established significant H<sub>2</sub>-binding enhancement by metal atoms on nanotube-substrates, with up to 4-7% gravimetric capacity. Identified a problem of low-barrier to metal diffusion and potential metal aggregation, Figure 2. Discovered that metal binding strength depends on nanotube chirality and possibly on metallic versus semiconductor type.



**FIGURE 2.** Barrier for possible metal atom migration over the carbon nanotube surface may be low in certain cases, but metal aggregation is not excluded.

- Presented first 3D-foam obtainable (via welding process) from single-wall nanotubes (Figure 3). Demonstrated the *welding path* to this structure. This opens the way to engineering 3D structures with nanotubes as initial frameworks.
- Computationally established hydrogen-binding enhancement by metal-atom centers on SWNT-carrier, while the low ~0.2 eV diffusion barrier cannot prevent aggregation, causing storage reduction and remains an issue.
- A chemically cross-linked 3D-framework (Figure 4) is analyzed for stability with quantum-chemistry



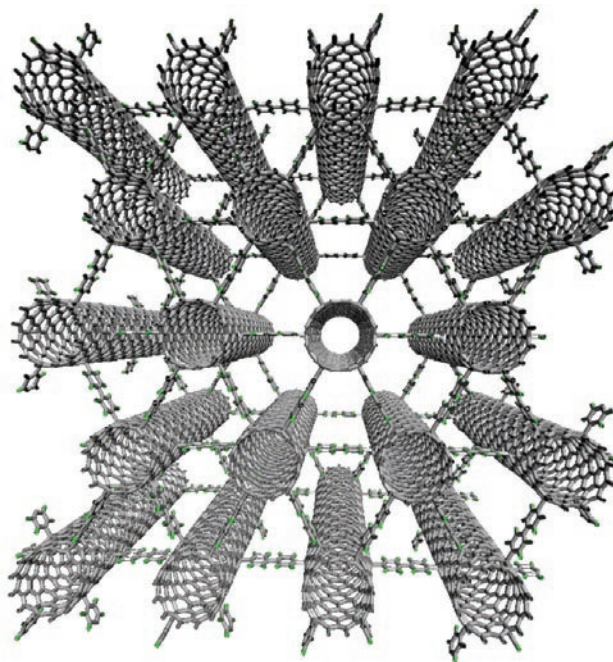
**FIGURE 3.** A small sample of carbon foam derived by welding of an array of (5,5) and (10,0) nanotubes, shows high surface area with full accessibility to diffusion.

methods. Both show high accessible area with potential to reach DOE targets for storage.

- Brought HiPco production to stable operational conditions at above 1 g/hr rate; control of SWNT diameter is achieved.

#### Partner FY 2007 Plans

- Calculate the chirality and diameter dependence of the binding energy for a single metal atoms or small clusters on a SWNT and graphene surface. Study the aggregation behavior of the metal atoms, the corresponding dependencies on the type (chirality and diameter) of the SWNT. Study the hydrogen storage ability on the aggregated metal clusters. Find possible ways to stabilize the atoms of metal (e.g. by creating topological or other types of defects).
- Determine configurations and aggregation-barriers of metal complexes on SWNT. Screen through broader series of metal atoms for sorption enhancement. Continue search for better interactive



**FIGURE 4.** A completely relaxed stable structure of a nanotube array, with the biphenyl cross links maintaining the proper (with possible further modifications) spacing to ensure accessibility of the tube exterior for better storage.

potential of H<sub>2</sub> with metallic versus semiconducting nanotubes, and if there is distinguishable variability (some general method limitations here).

- Perform computations, within the same method and approximations, of the binding and mobility barriers for H on carbon. Design simplest model for the metal/carbon contact and investigate energy barriers for hydrogen steps over this interface. Prepare the set of key quantitative parameters for spillover modeling.

#### Rice University, FY 2006 Publications/Presentations

1. MRS Fall Meeting, December 2005, Boston, presentation (delivered by R. Hauge).
2. FreedomCAR Tech Team meeting March 2006. Washington, D.C.
3. MRS Spring Meeting, San Francisco, April 2006, invited talk (B. Yakobson).
4. FY 2006 DOE Annual Merit Review, May 2006, Crystal City, VA (poster presentation).