

Theoretical Models of H₂-SWNT Systems for Hydrogen Storage and Optimization of SWNT Production

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Project ID #
STP17 Yakobson

Overview

Timeline

- **Start: 01 February 2005**
- **End: 31 January 2010**
- **18% complete**

Budget

- **Total project funding**
 - **DOE: \$857,998 (1.75M request)**
 - **Contractor: \$216,476**
- **Funding in FY05 \$75,000**
- **Funding for FY06 \$175,000**

Barriers

Barriers to be addressed

- **Develop flexible representation for hydrogen-carbon non-chemical binding (van der Waals forces)**
- **Recommend optimal nanotube types for hydrogen retention**
- **Identify carbon-based geometries for the best physisorption**
- **Identify role of metal in hydrogen retention**

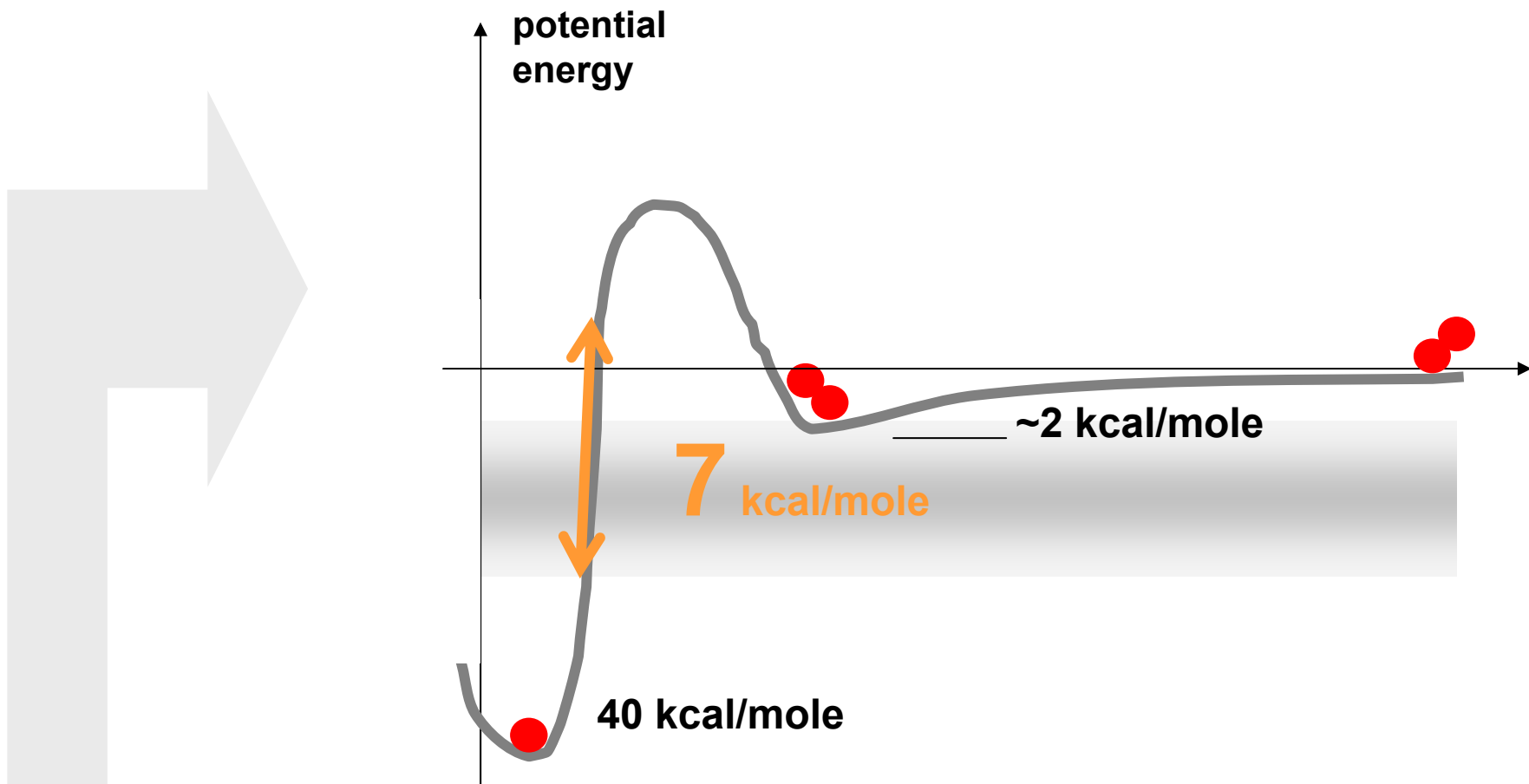
Partners

- **NREL, Air Products Corp,** regular teleconferences, face-to-face meetings (Houston, Lucca, Boston, Houston, Washington, Gaithersburg, MRS San Francisco).

Objectives

- **Overall:** Develop predictive models of materials structures interaction with hydrogen, in order to optimize their makeup for storage and assess the gravimetric and volumetric capacity. Provide recommendations for the synthetic goals (e.g. diameter, type and organization of SWNT).
- 2005: Theoretically investigate transition-metal enhanced adsorption via the various ways of doping carbon backbone $\text{Me@C}_n + m^*\text{H}_2$, Me = Sc, Ti, ... or Li, K.
- Investigate role of diameter and chirality on Me binding, and the highest gravimetric capacity.
- **2006:** Explore full utilization of physisorption by van der Waals dispersion forces. Develop and perform optimization of pure carbon carrier geometries for best **surface, accessibility, and retention capacity -- binding energy**.
- Use **HiPco** method to produce nanotubes of preferred diameter (and length) for better hydrogen adsorption.
- Perform quantum mechanical computation for precise description of van der Waals attraction. Compute potential wells for H_2 -trapping on generic carbon structures, for achieving 7-8% storage.
- **2007:** Investigate effects of elastic and inelastic curvature of carbon cages on the strength of van der Waals attraction and develop proper force-field correction. Compute hydrogen capacities (gravimetric and volumetric) as function of pressure P and temperature T.
- For the ideal carrier geometry, to assess at what P,T the capacity of 7-9% can be reached, that is to establish theoretical limits for storage on pure carbon carriers.
- Explore mixed (chemical/physical) sorption mechanisms, and the role of hydrogen spillover storage.

Background and Challenge: Hydrogen for Energy Storage

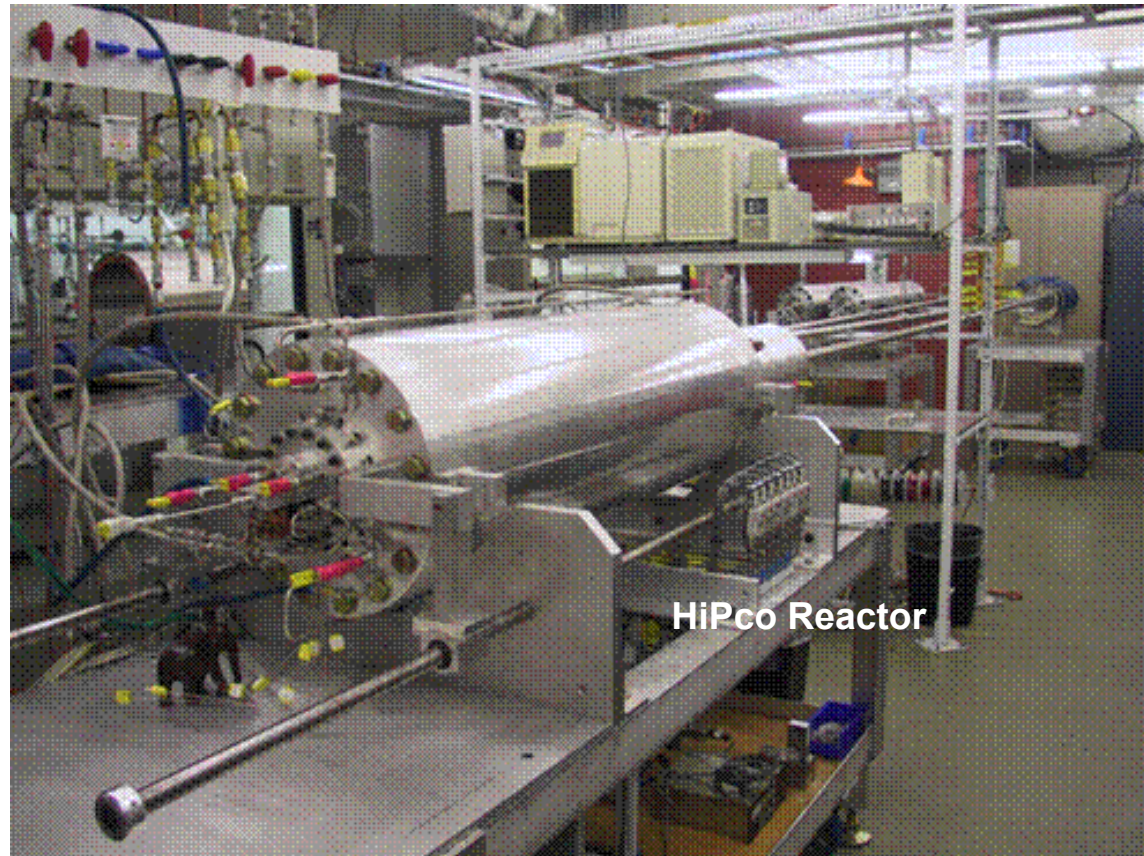


Generic H₂-substrate attraction is either too weak or too strong.

To meet the DOE gravimetric goal of ~6-8%, the binding energies ~7 kcal/mole need to be achieved for the carbon-based carrier material. This can be attempted by the static or dynamic curvature, local electrical fields, and/or possible role of dopants.

Background of the HiPco nanotube production

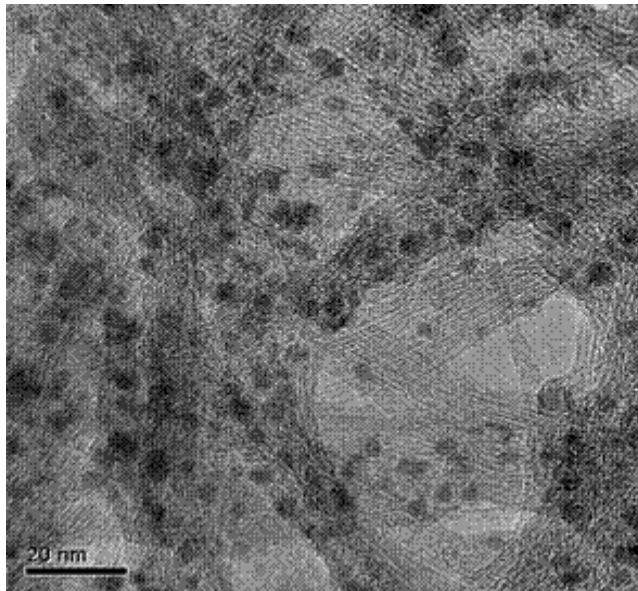
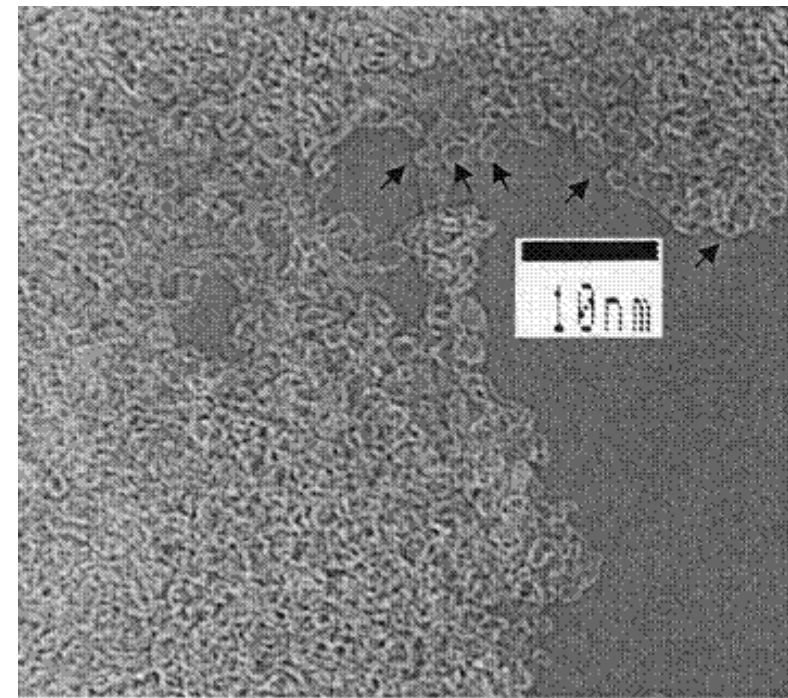
- High Pressure CO at ~ 1000 °C is mixed with room temperature gas containing iron pentacarbonyl
- Standard operating conditions are iron carbonyl at 52 mtorr in the reactor with an overall reactor pressure of 30 atm with a CO recirculating flow rate of 550 slm.
- Iron clusters form and catalyze the Boudouard reaction
 $2 \text{CO} \rightarrow \text{CO}_2 (\text{g}) + \text{C} (\text{s})$
- Nucleation and growth of SWNT occurs in milliseconds near the point of mixing
- The SWNT is filtered out and the CO is recycled and CO_2 removed to create a continuous process



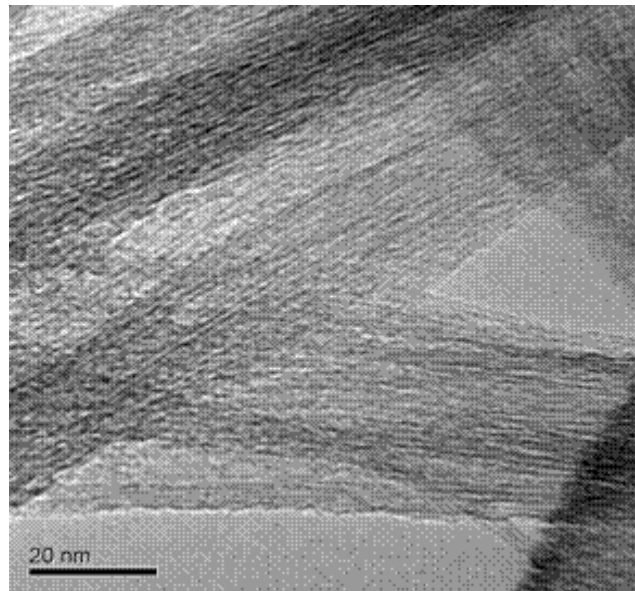
Approach

HiPco nanotube product will be optimized for use as constituent structure for high capacity hydrogen storage

Large fullerenes extracted from raw HiPco sample by fluorination



Raw tubes, with residual Me-catalyst



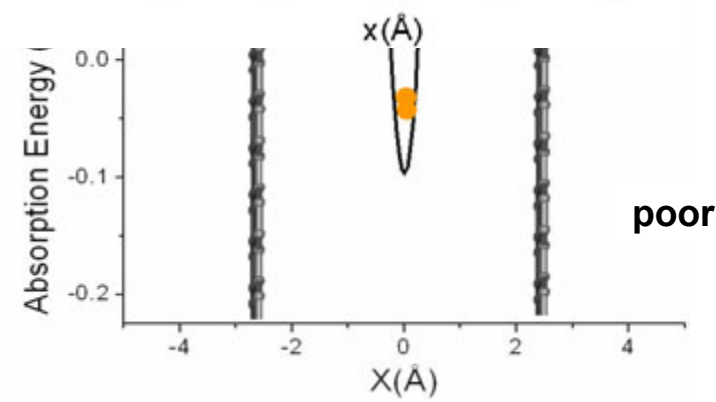
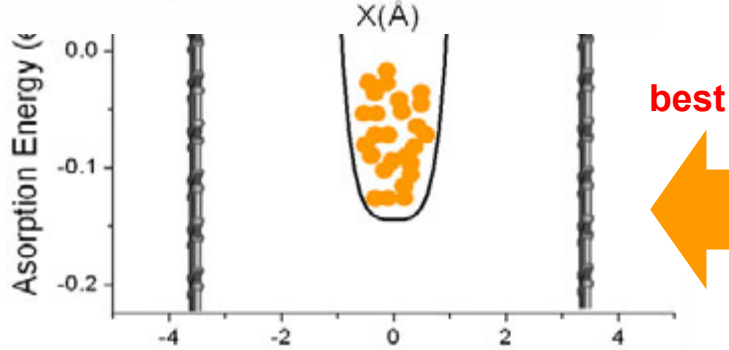
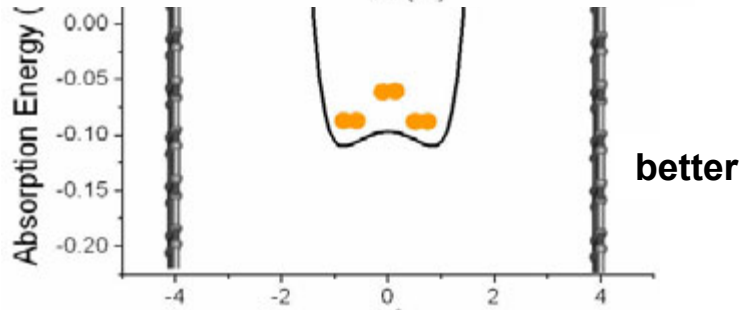
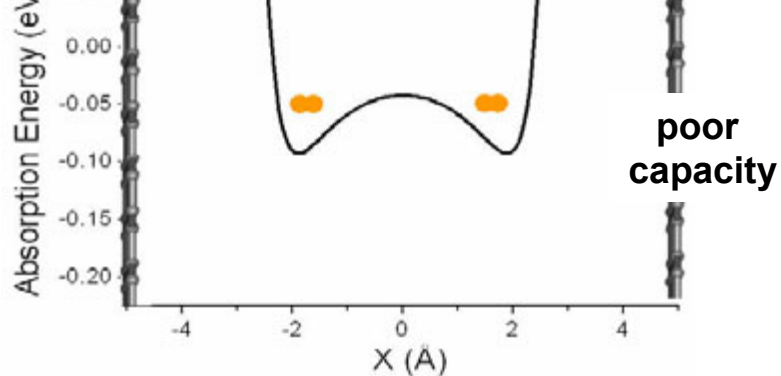
Cleaned tubes

Example TEM images

Approach

Develop adequate modeling tools for hydrogen storage assessment and optimization of carbon-carrier makeup. Achieve best binding of hydrogen by designing proper geometrical confinement in the nanotube-derived structures.

← Example: graphene double-layer

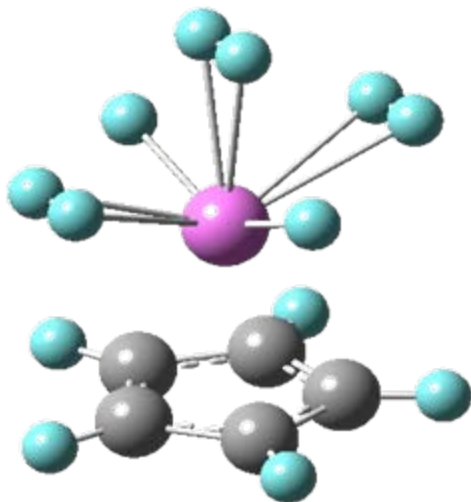


H₂-----carbon potential optimization

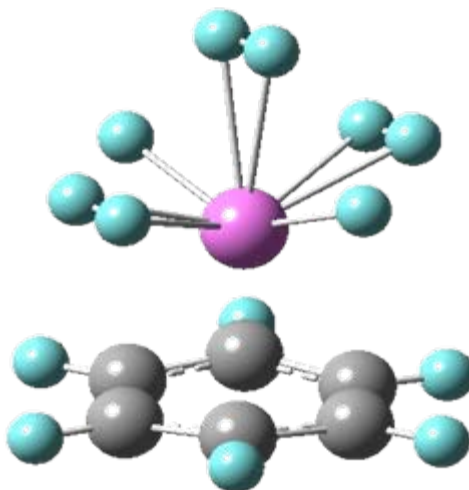
Superposition of the potentials can enhance adsorption at the **optimum spacing**

Approach

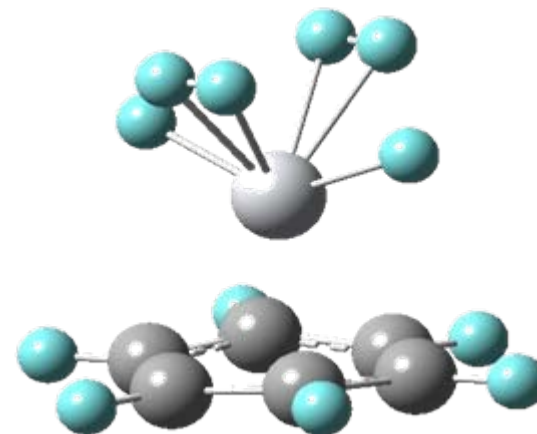
Develop quantitative models for assessment of the binding enhancement by metal atoms on carbon nanostructures. Examples: Sc or Ti on carbon site



A: Sc-pentagon
w,%(H₂) = 6.8%



B: Sc-hexagon
w,%(H₂) = 6.1%



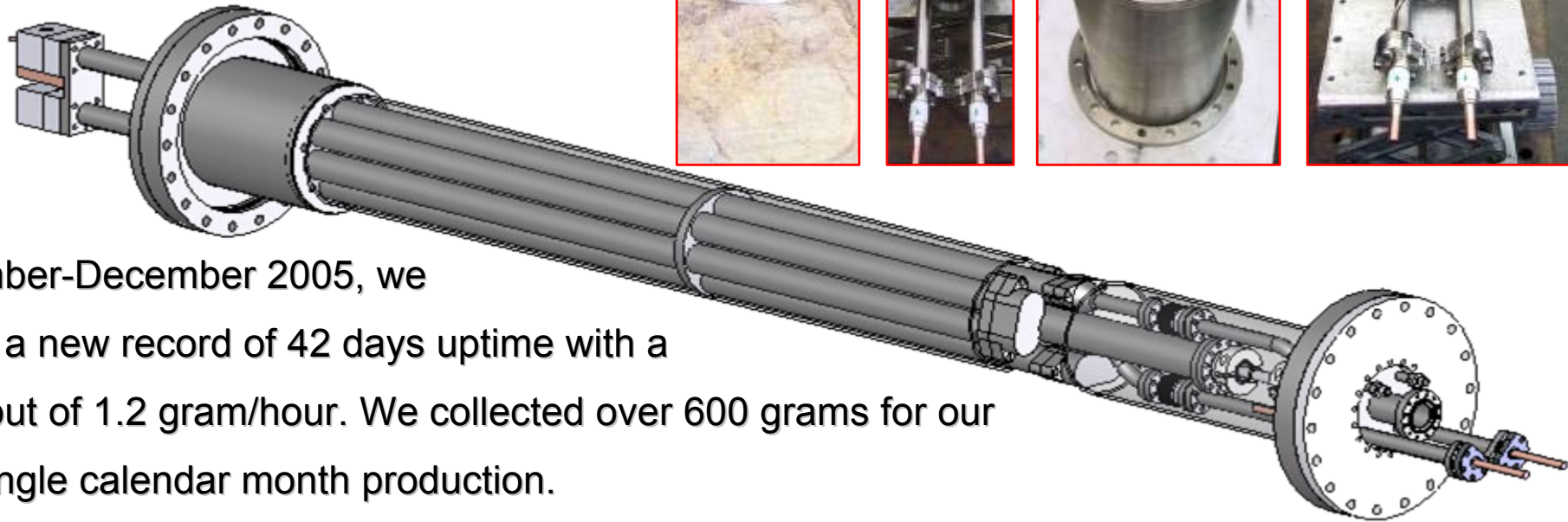
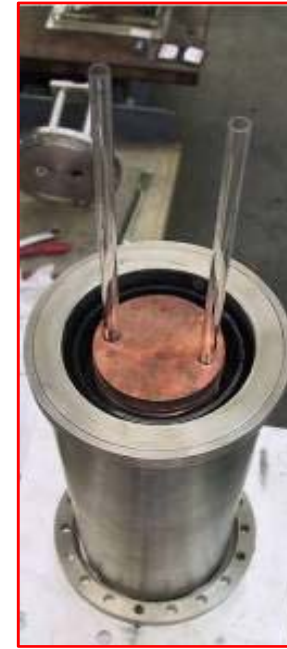
C: Ti-hexagon
w,%(H₂) = 4.5%

Structure	Binding energy of each hydrogen molecule, eV			
	1 st (dissociated)	2 nd	3 rd	4 th
A	1.554	0.132	0.118	0.026
B	0.822	0.067	0.177	0.065
C	0.799	0.222	0.347	none

Technical Accomplishments

HiPco @ Rice

A *scalable continuous* process for SWNT production.
World's best quality SWNT supply for fiber spinning.
1+ month continuous runtime at 1 gram/hour
production rate.



In November-December 2005, we
achieved a new record of 42 days uptime with a
Throughput of 1.2 gram/hour. We collected over 600 grams for our
largest single calendar month production.

Fully automated reactor produces consistent product for nanoengineered H₂ storage media

Technical Accomplishments

Process studies

Catalyst nucleation aides

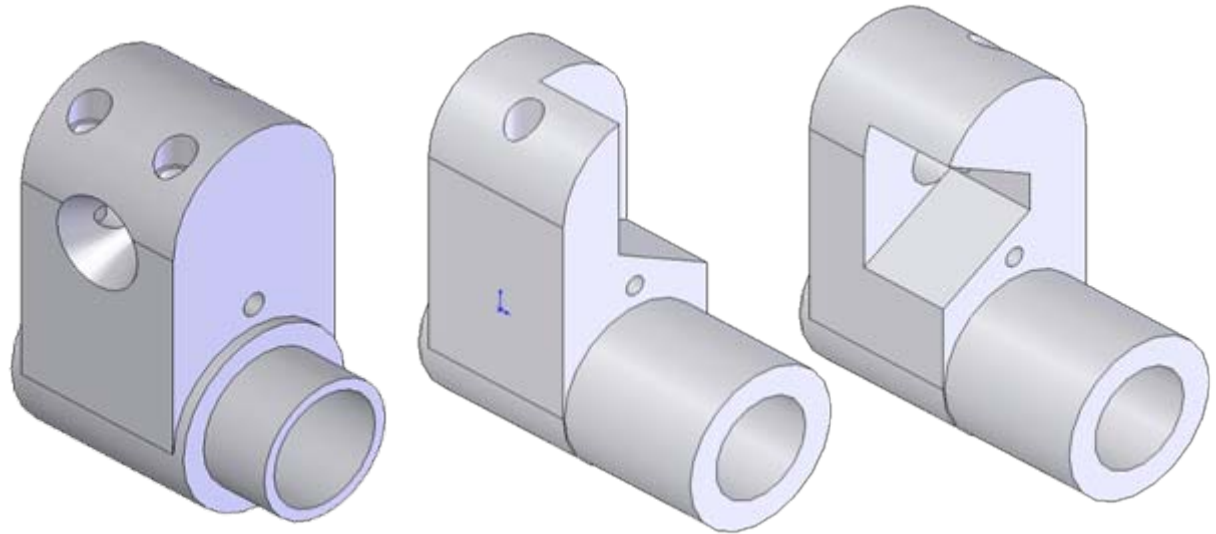
- Added various proprietary chemicals to enhance nucleation.

Process Conditions

- Temperature
- Concentration
- Flow rates

Mechanical Tweaking

- Experiments have been made to alter the mixing time and product flow path to prolong growth mechanism.



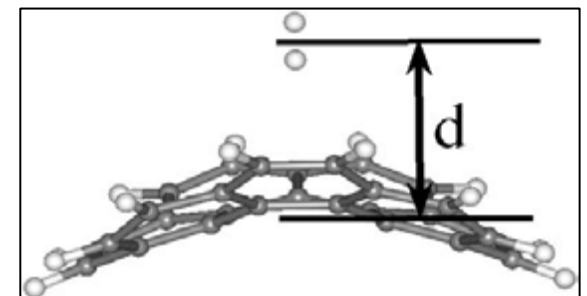
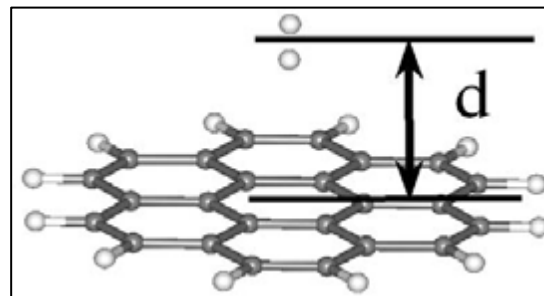
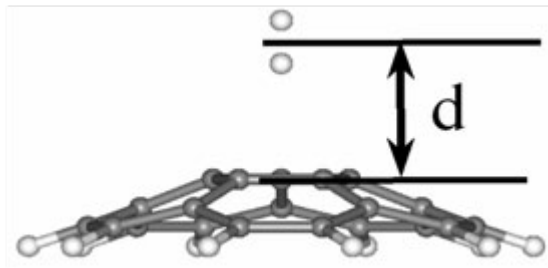
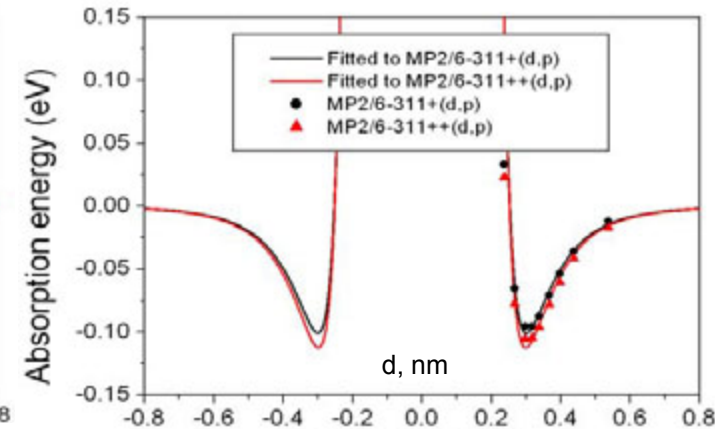
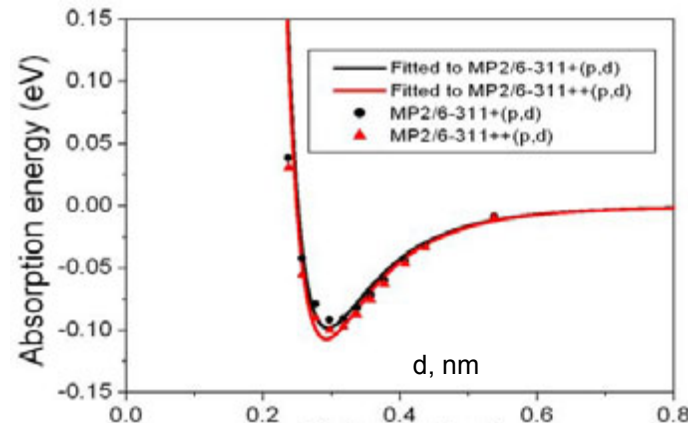
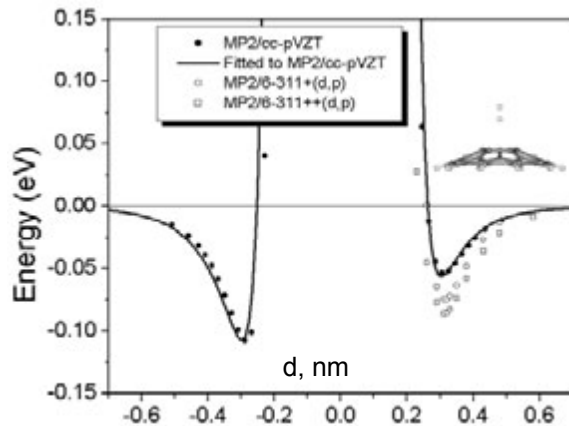
Special Design Mixers

Hot CO mixes in two parts with catalyst containing cold CO, creating an intermediate temperature and resident time for pre-clustering. This provides more control over catalyst size and hence the properties of the SWNT that are produced.

The flexible HiPco reactor design provides for continuing research on controlling the quality, length, diameter, and chirality of nanotubes that become the feedstock for the spun fiber and subsequent nanoengineered H₂ storage media.

Technical Accomplishments

Force-field parameters of van der Waals interaction with basic topological defects in graphene are derived from quantum MP2 calculations*

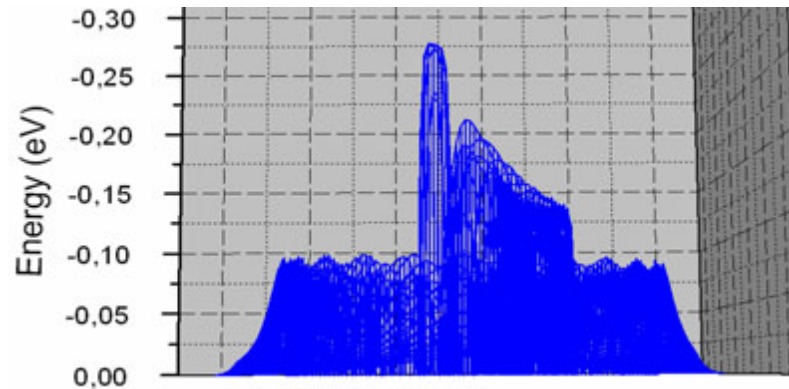
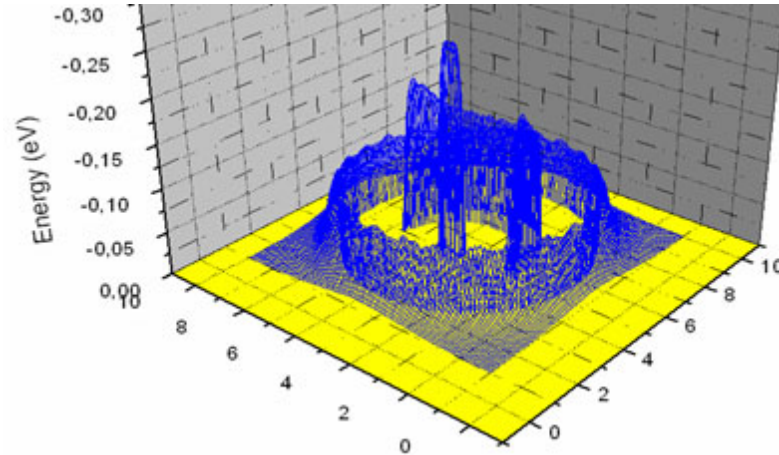
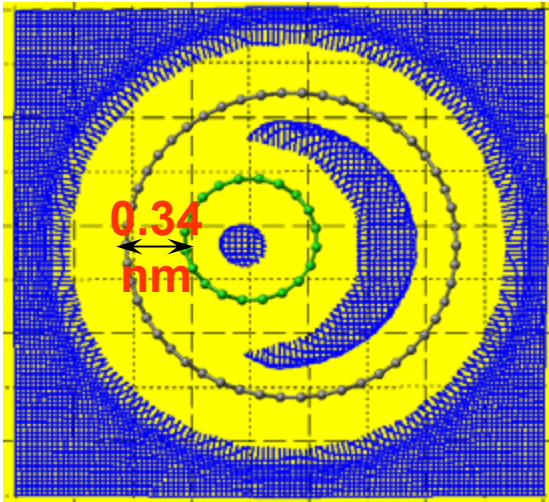
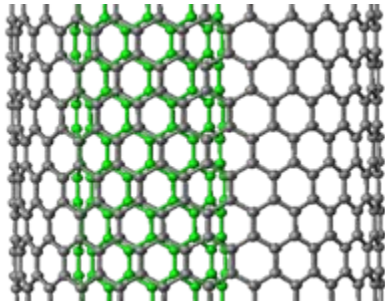


The van der Waals parameters show weak dependence on the topological defects and can be accounted for. Very large curvature can add curvature-dependent chemisorption component. This is first step to the rapid storage-potential computing.

*) MP2 is Møller-Plesset second-order perturbation theory

Technical Accomplishments

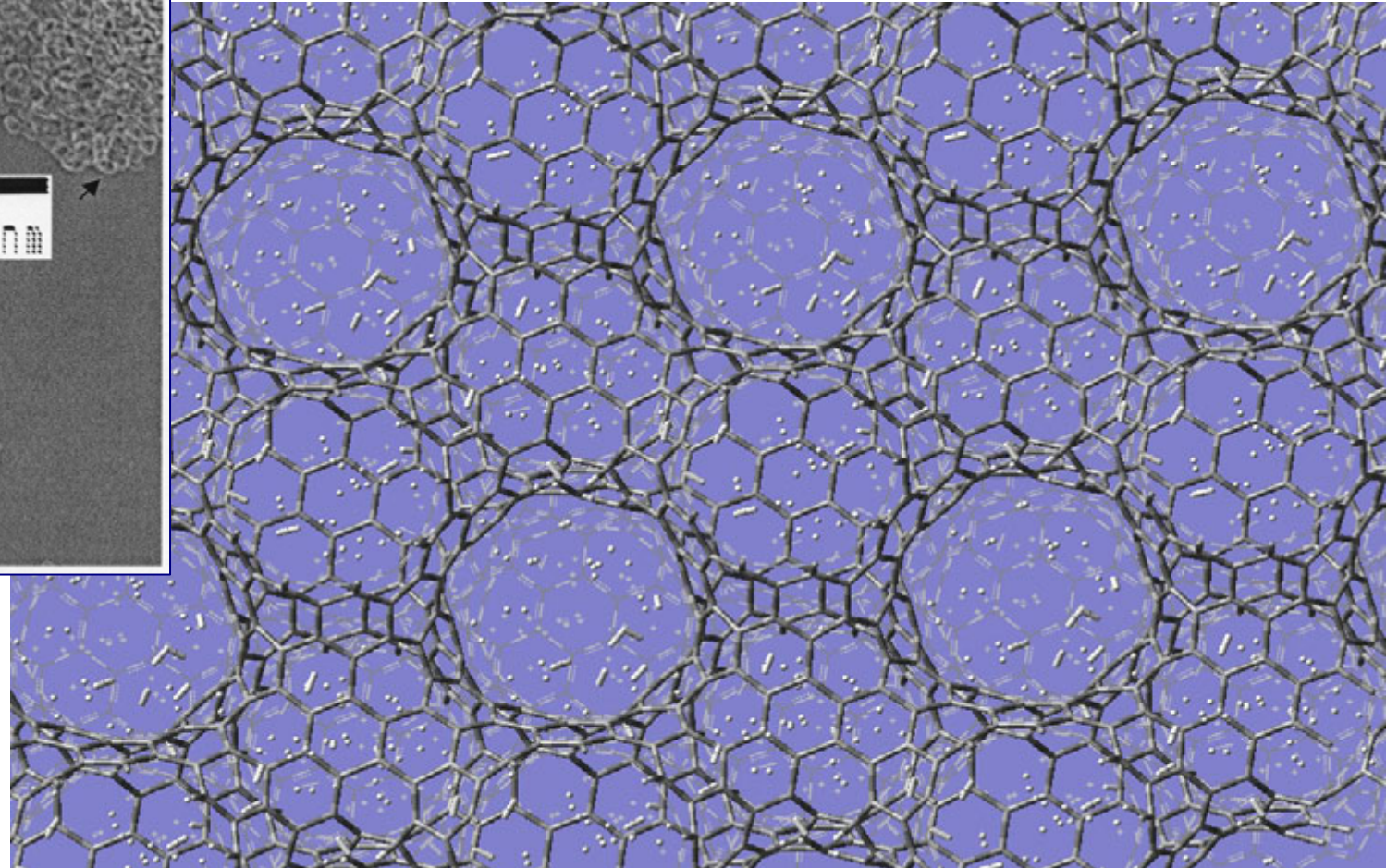
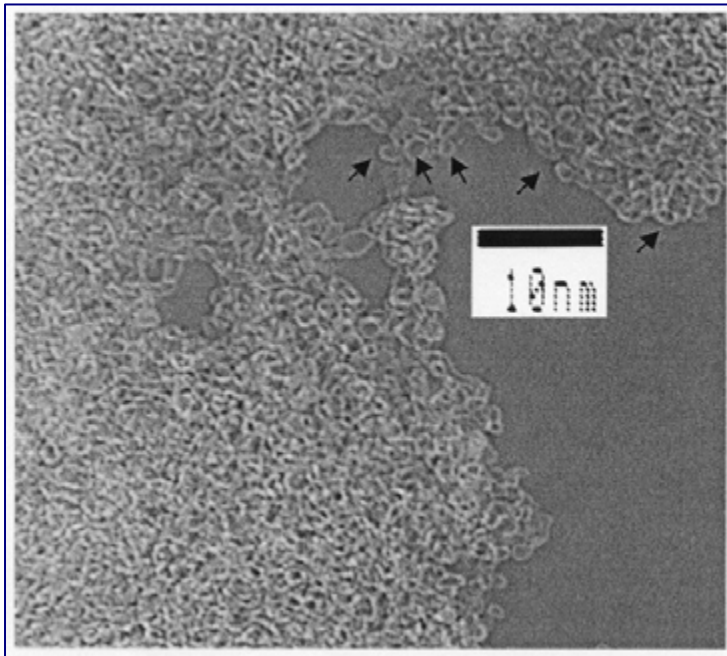
“Rapid prototyping” of potential wells: double-wall NT example



Potential wells for hydrogen trapping can now be efficiently computed for the variety of trial structures.

Technical Accomplishments

Example of carbon foam structure for hydrogen storage, designed from the buckyballs or larger fullerenes, by their annealing/welding process. Large size structure is optimized with semiempirical quantum-chemical method. It is stable, mechanically robust and highly porous.



C₆₀-based carbon foam
density 1.3 g/cm³
H₂ uptake up to 65 g/L at w =
5% gravimetric capacity

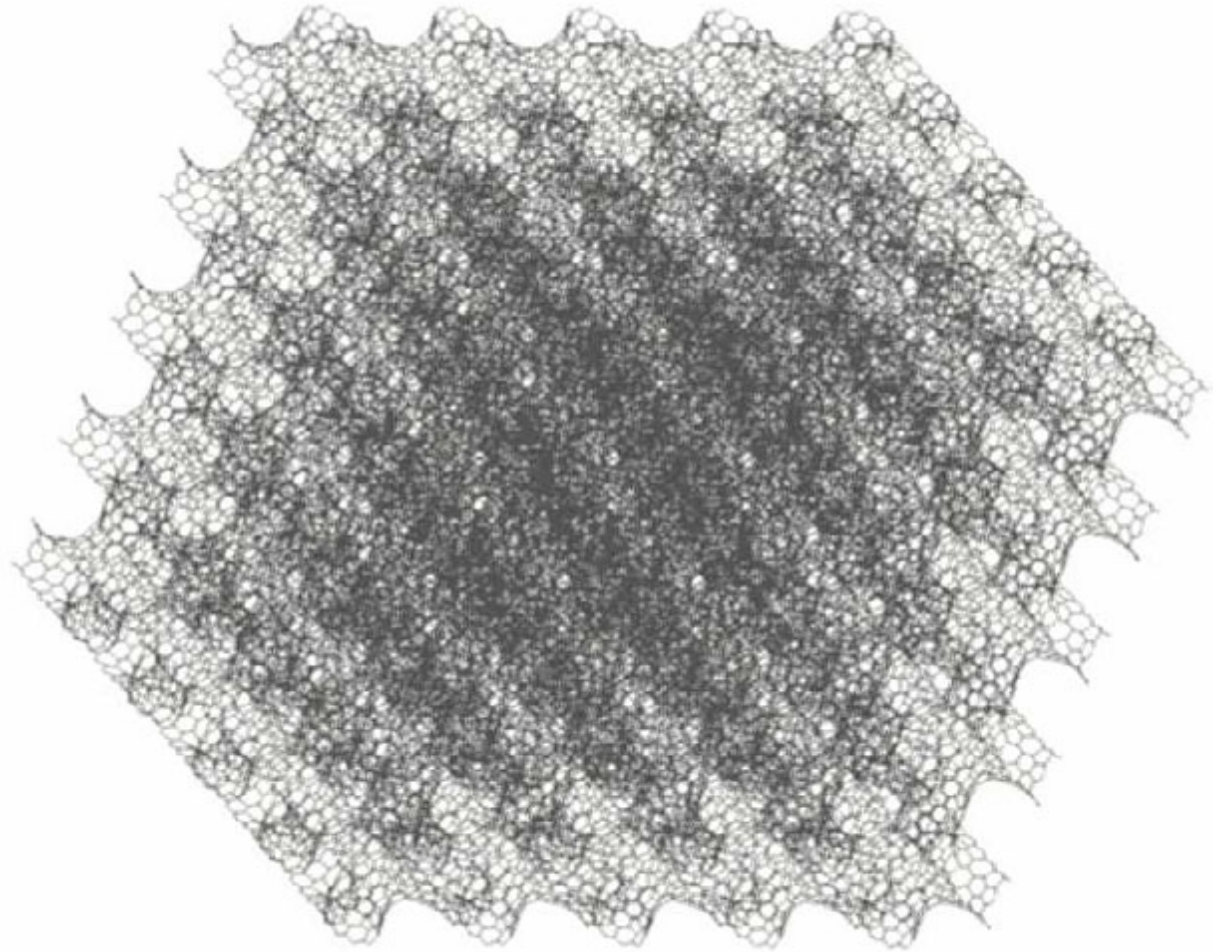
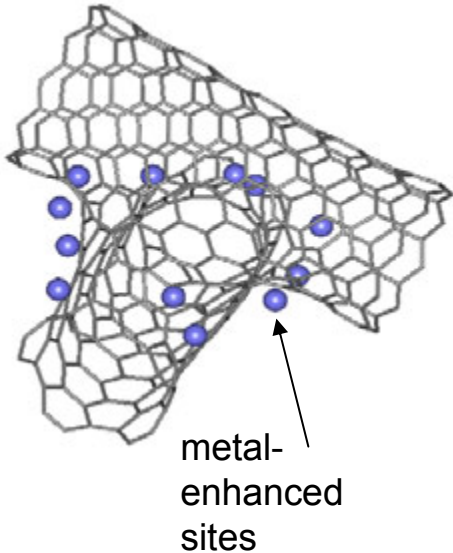
Technical Accomplishments

3D carbon foam designed by high T annealing-welding of SWNT. Large size structure is optimized with Tersoff-Brenner potential.

here $\sim 1000 \text{ nm}^3$
40,000 atoms
3000 heptagons
 $\sim 15\%$ of all

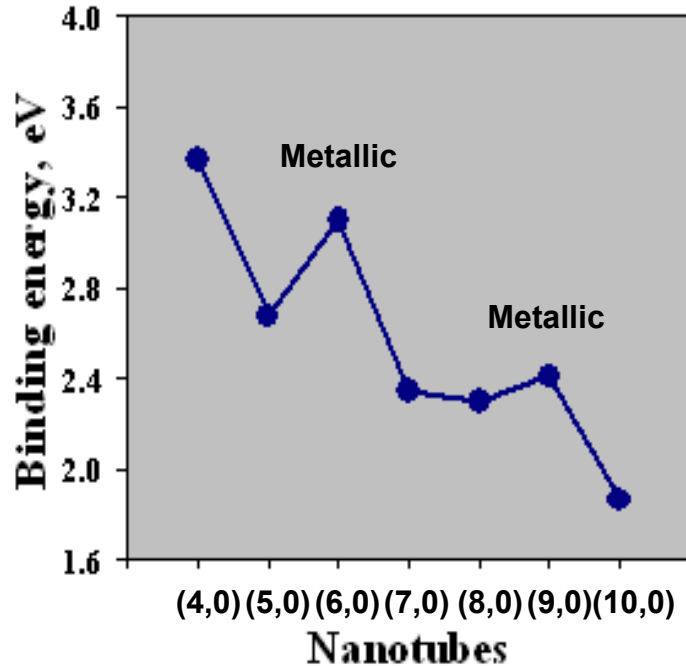
density $\sim 0.9 \text{ g/cm}^3$

surface $2600 \text{ m}^2/\text{g}$
up to $w = 7\%$, wt storage
to 63 g/L

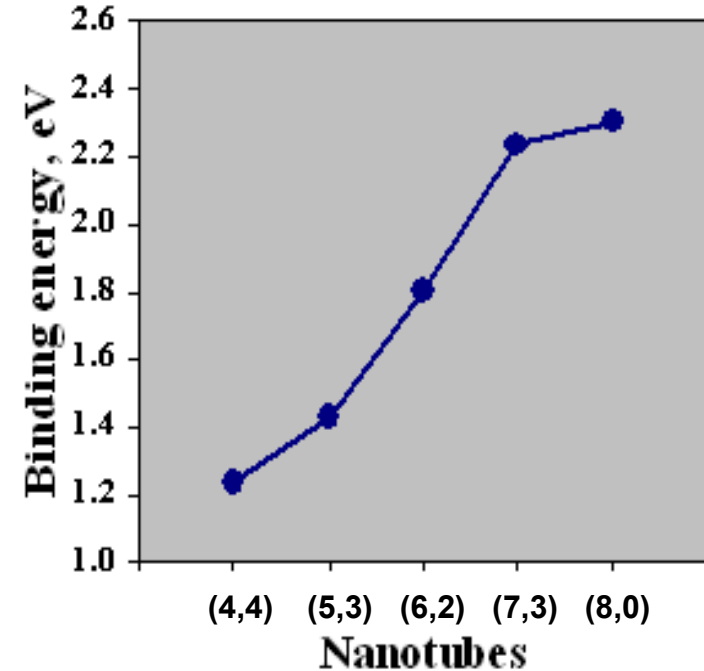


Technical Accomplishments

Evaluated stability of the Me-sites. E.g., binding energies of Sc with SWNT:



Diameter dependence of the interaction energy between Sc and SWNT(m,0), with m=4 to 10



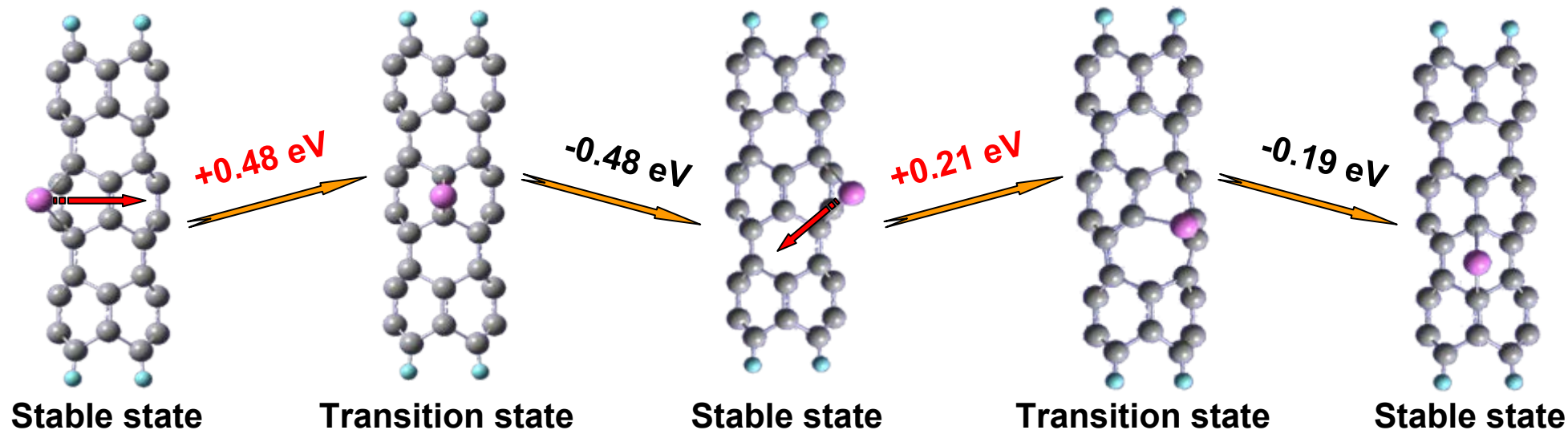
Chirality dependence of the interaction energy between Sc and SWNT(m,n), with m=4 to 8 and n=8-m

Interaction of the Sc with graphene layer: **~0.20 eV**.

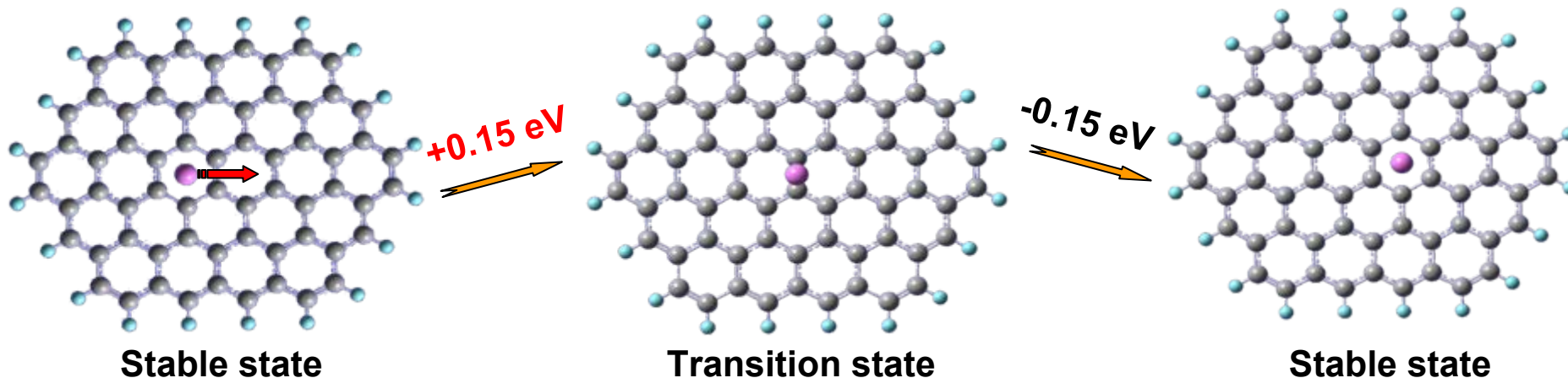
Established: metal-tube interaction is sensitive to the tube diameter and chirality. Higher binding energy is achieved on small zigzag tubes.

Technical Accomplishments

Investigated mobility of Me atoms on carbon nanostructures

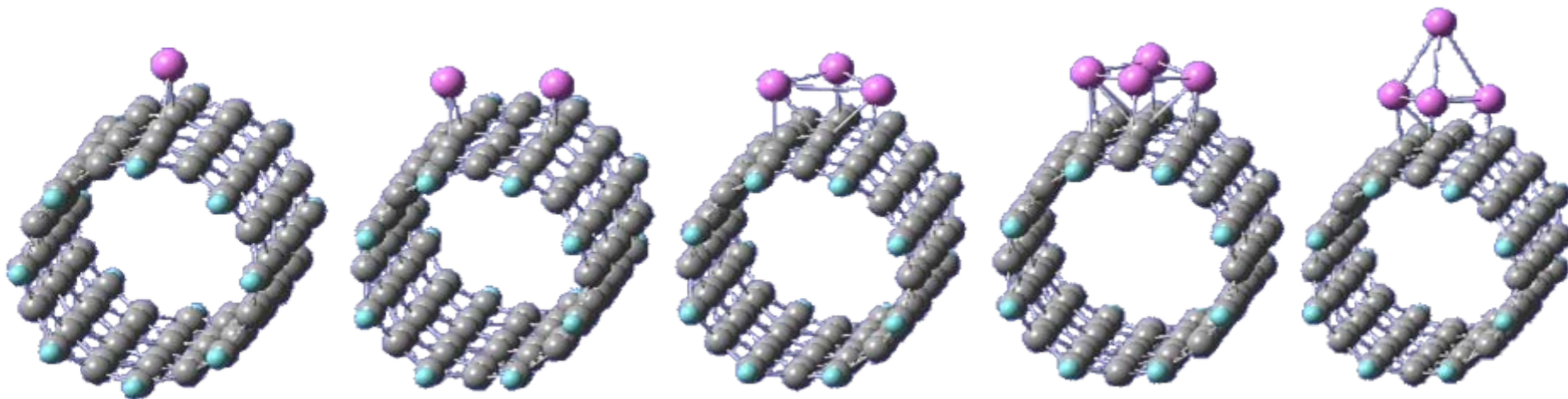


Potential barrier of Sc diffusion along SWNT (4,0) and along graphene layer



Low potential barriers indicate possibility of metal aggregation, detrimental for storage

Technical Accomplishments



Per Sc: 2.303 eV

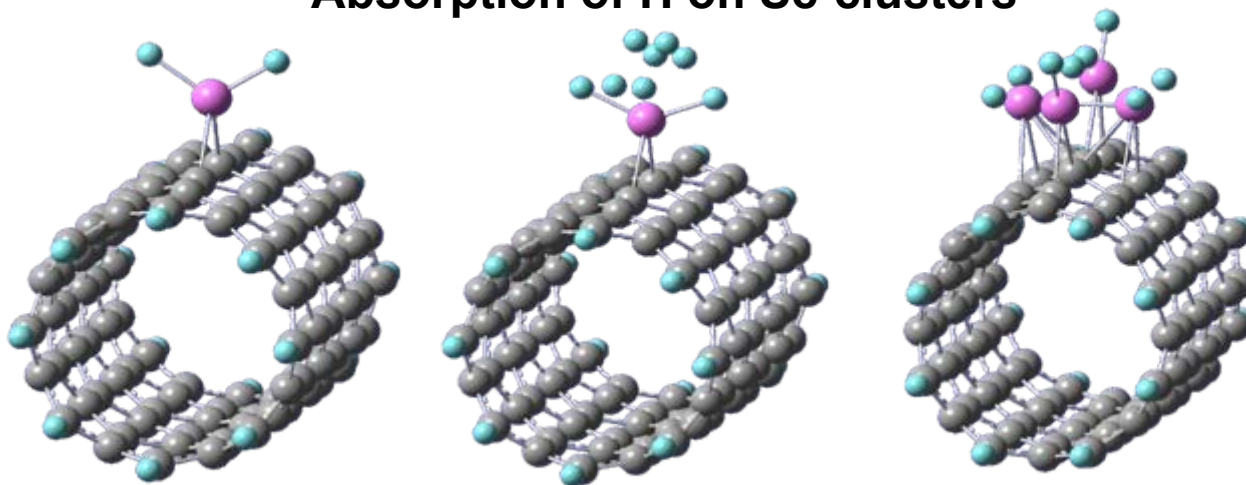
2.439 eV

2.522 eV

2.453 eV

2.353 eV

Absorption of H on Sc-clusters



0.88 eV per H₂

0.24 eV per H₂

1.48 eV per H₂

Aggregation of Sc atoms on the SWNT surface is shown to reduce the hydrogen storage capacity

Future work

1. **Optimize the reactor to produce SWNT of the highest purity, best uniformity and the optimum diameter needed for hydrogen storage media.** FY07.
2. **Search for the best *metal-on-carbon* for hydrogen retention Calculation of the metal ability to bind H₂.** FY06.
3. **Theory of hydrogen storage enhancement via spill-over** FY07, in collaboration with R Yang.

Specific questions to be addressed:

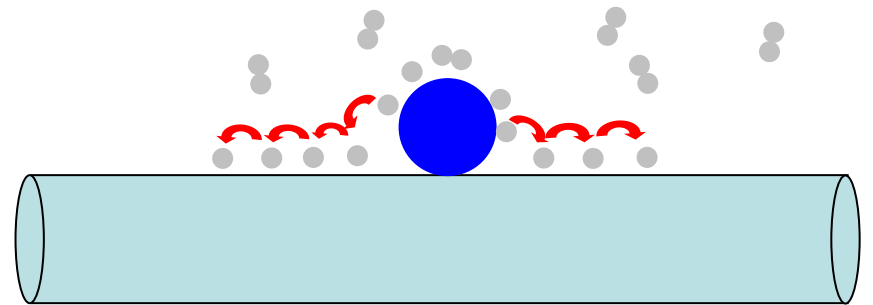
Catalyst metal cluster and CNT interactions.

H₂ dissociation on the catalyst atom/cluster surface.

The diffusion of H from metal surface onto CNT.

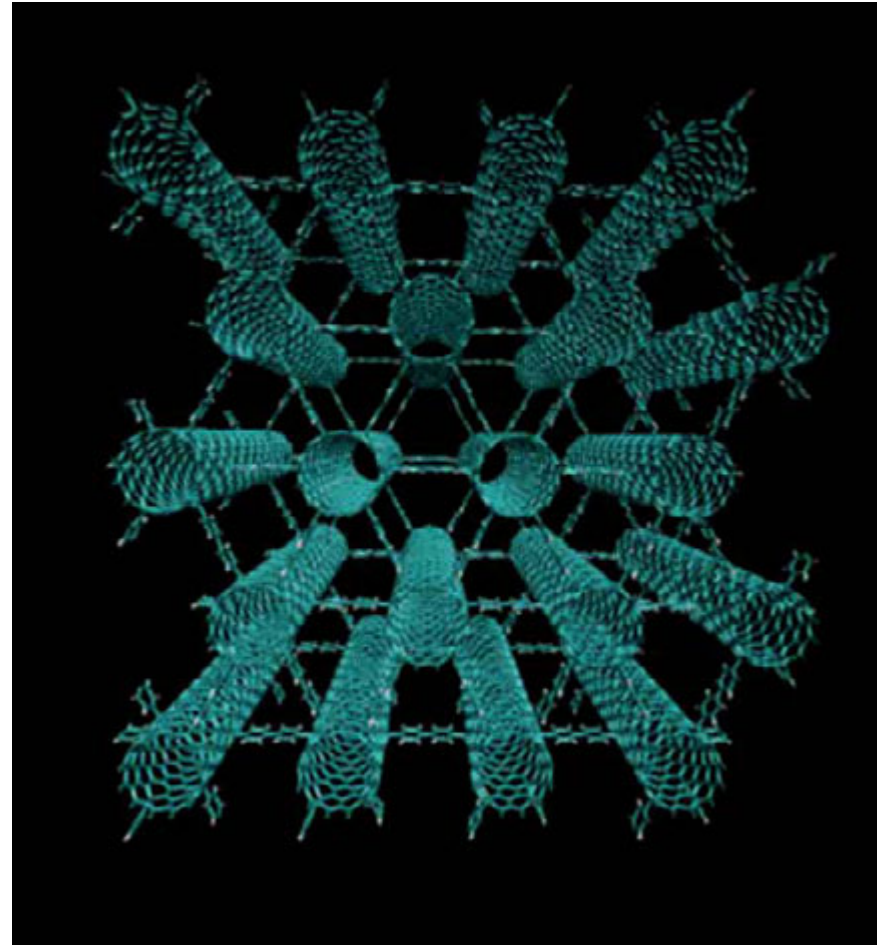
The absorption energy and diffusion barriers of H on CNT surface.

The release of hydrogen – how the spillover can be reversed?



Future work

3. Further refinement of van der Waals force-field, with an eye on topological and elastic curvature effects.
4. Develop statistical-thermodynamics model for H_2 “pumping” into potential wells provided by carbon-based carrier material.
5. Assess hydrogen storage of the carbon-based foams, cross-linked arrays-bundles, and other structures. Predict optimal geometries.



Summary

1. HiPco production is brought to stable conditions in daily operation, presently above 1 g/hr rate, with over a month of uninterrupted work. Control of diameter of the produced SWNT is achieved, and must be further improved.
2. Computation establish significant hydrogen binding enhancement by metal-atom centers on carbon nanotube carrier, with up to 4-7% gravimetric. Low barriers for Me diffusion cannot prevent aggregation into clusters at elevated temperatures, with possible reduction of hydrogen storage. Broad range of Me-component must be further explored.
3. Designed and computationally verified stability of nanotube-derived carbon foams, 3-dimensional self-supporting material with high surface area $\sim 2600 \text{ m}^2/\text{g}$, and gravimetric capacity up to 7% with 63 g/L [example of (10,0)-SWNT foam]. Exact thermodynamic model for H_2 retention in the foams should be further developed for predicting the storage capacity $w(P,T)$ at various conditions.

Summary Table

On-Board Hydrogen Storage System Targets

****Data is based on HiPco produced material only, not system value; parameters for optimized designed foam- and Me-enhanced structures can/will be computed upon completion of thermodynamic model**

Storage Parameter	Units	2010 System Target	FY05 materials**	FY06 Result materials**
Specific Energy	kWh/kg (wt% H ₂)	2.0 (6 wt%)	0.43 1.3 wt%	0.97 2.9 wt%
Volumetric Energy Capacity)	kWh/L	1.5	0.43	0.97
Desorption Temperature?			>77 K	>77 K
Plateau Pressure			Measured at 2 bar	Fit to 30 bar

Publications

1. F. Ding, P. Krasnov, B. I. Yakobson, "Topological defects dependence of hydrogen absorption on graphene layer: Comparison of physical and chemical absorption" in preparation for Chem. Phys. Lett., 2006.
2. F. Ding, P. Krasnov, B. I. Yakobson, "A single wall carbon nanotube based foam structure for hydrogen storage", in progress.
3. P. Krasnov, F. Ding, B. I. Yakobson, "Aggregation of light transition metal atoms on carbon nanotubes and effect on the hydrogen storage", on preparation for J. Chem. Phys.
4. 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., Continued growth of single-walled carbon nanotubes. *Nano Letters* 2005, 5, (6), 997-1002.
5. Y. Zhao, B. I. Yakobson, and R. E. Smalley, "Dynamic Topology of Fullerene Coalescence", *Phys. Rev. Lett.* **88**, 185501 (2002).
6. A. K. Sadana, F. Liang, B. Brinson, S. Arepalli, S. Farhat, R. H. Hauge, R. E. Smalley and W. E. Billups "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." *Journal of Physical Chemistry B*, 109 (2005) 4416.