Optimization of SWNT Production and Theoretical Models of H_2-SWNT Systems For Hydrogen Storage

Carried out in the DOE Center of Excellence on Carbon-based Hydrogen Storage

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Rice University

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Project ID #STP38

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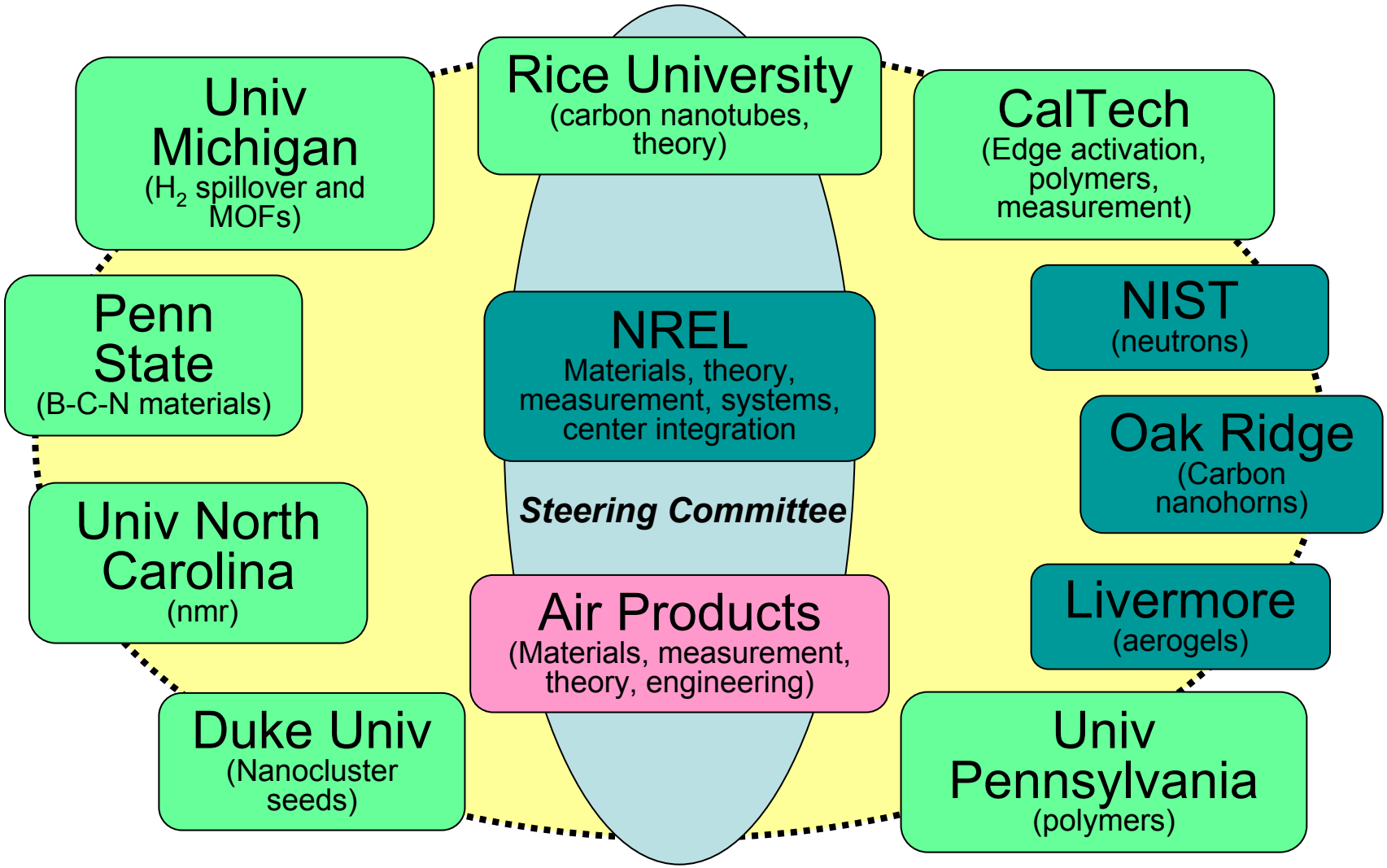
CbHS Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner



Optimization of SWNT Production and Theoretical Models of H_2-SWNT Systems for Hydrogen Storage

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General Objectives:

To produce single wall carbon nanotubes by the HiPco process that are optimal for molecular hydrogen adsorbtion

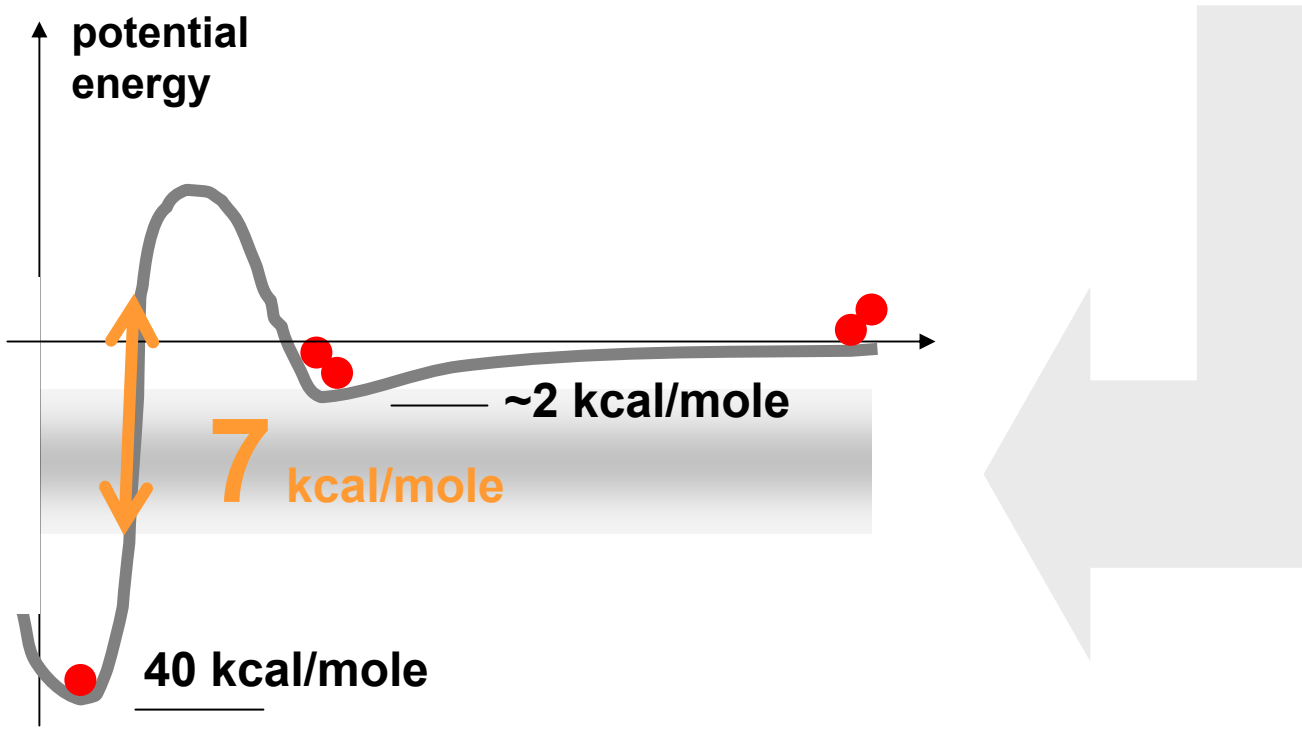
To expand theoretical analysis and computations of hydrogen interaction with carbon nanotubes produced at Rice by HiPco technology.

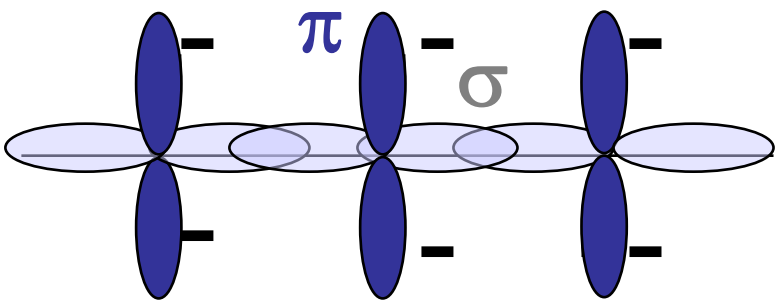
Obtain quantitative maps of binding energies for various chiral and diameter types of SWNT.

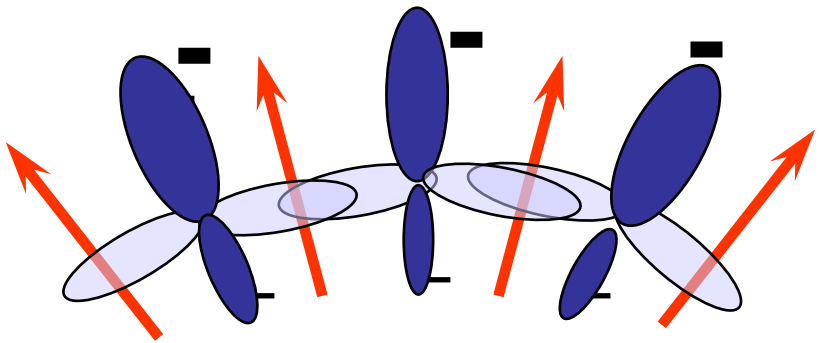
To derive recommendations, wherever possible, upon the best diameter and/or chirality of the HiPco SWNT

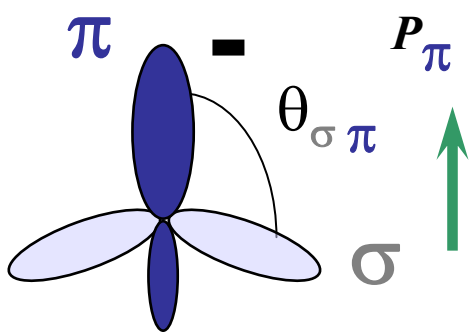
Challenge:

Can the desirable range of binding energies be achieved for some types of nanotubes, due to their static or dynamic curvature, local electrical fields, and/or possible role of metal-dopant?





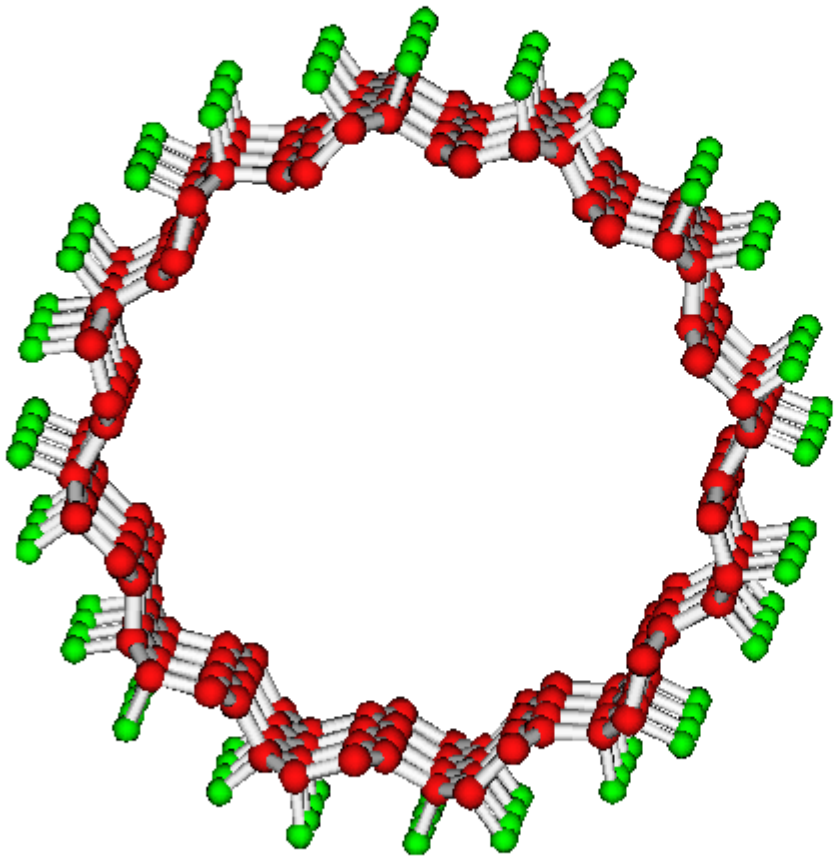




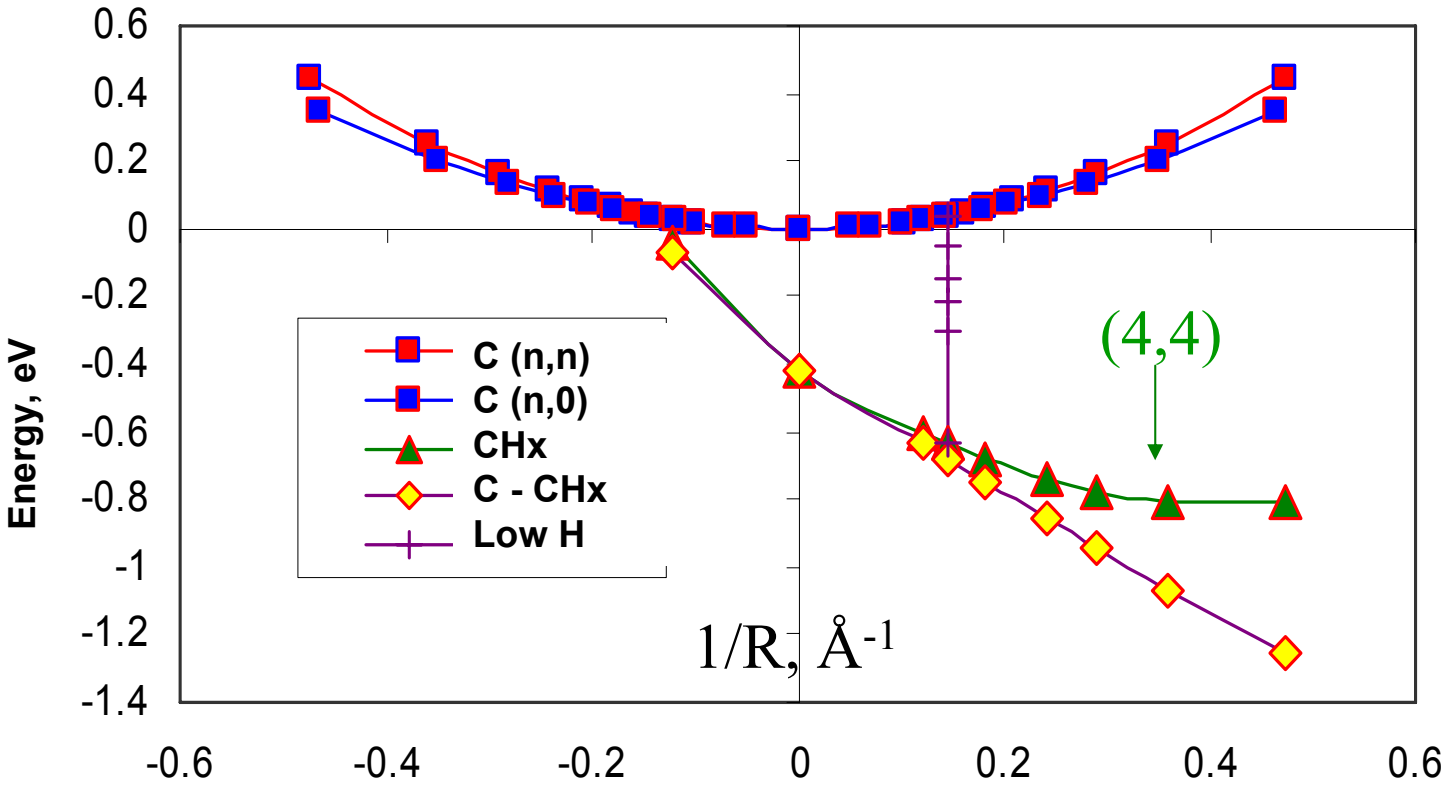
Will further explore curvature-induced polarization and evaluate local field and their ability to change the energy of physisorption

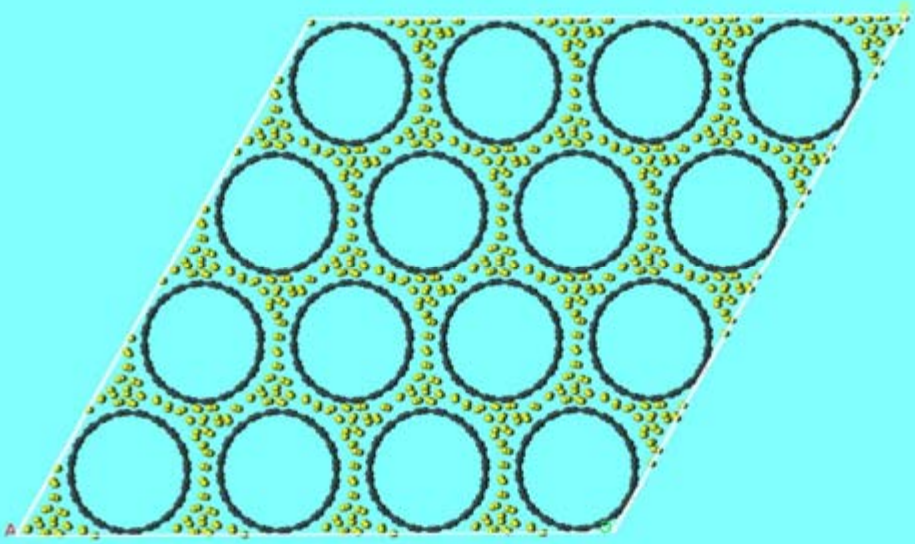
Preliminary/past work
Yakobson *et al.*,
Chem Phys Lett v **360**, p 182

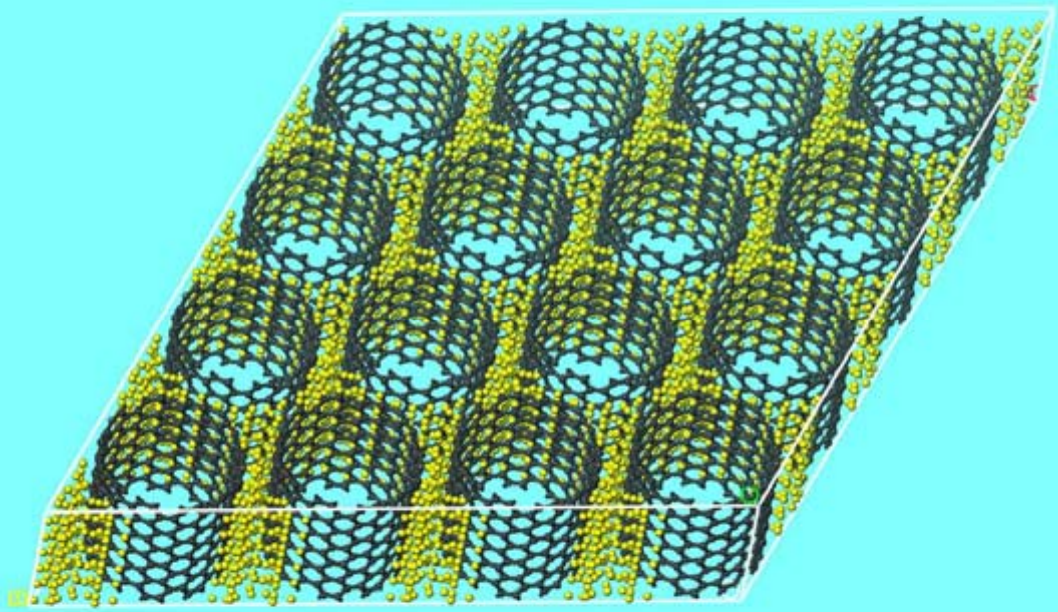
Compute binding energies and the “saturation limit” for nanotubes of different diameters and chiral types, for both exterior and interior attachment (shown here is armchair type)



Generate quantitative maps of binding energy as a function of radius (as shown here) and chirality, as a difference of total energies of pristine and H-saturated tubular structures

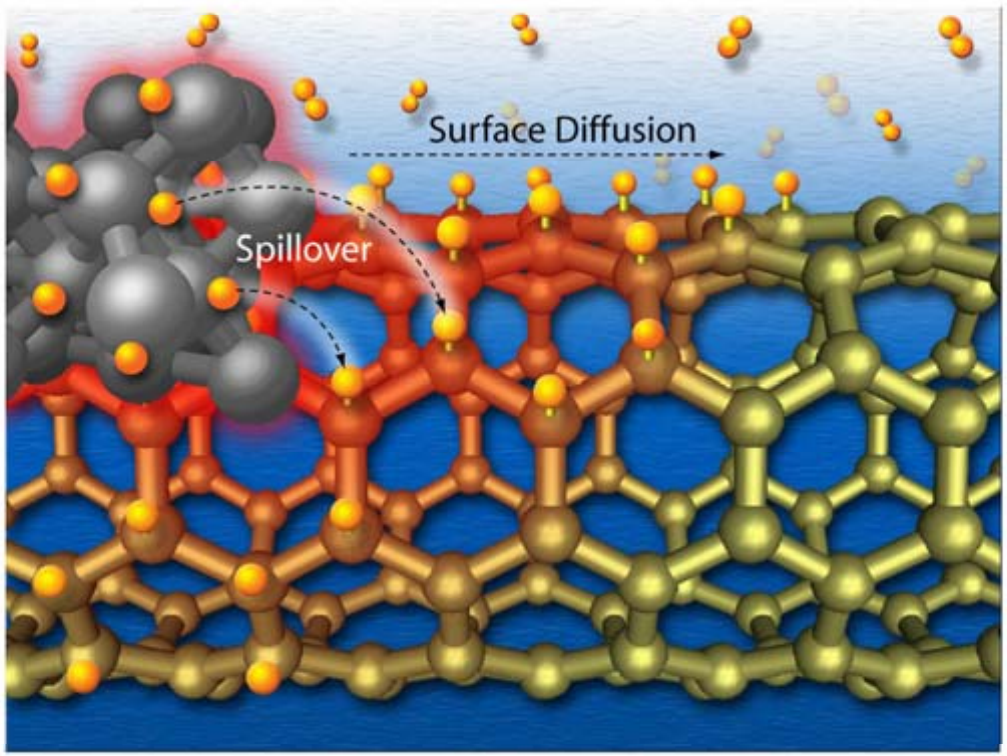






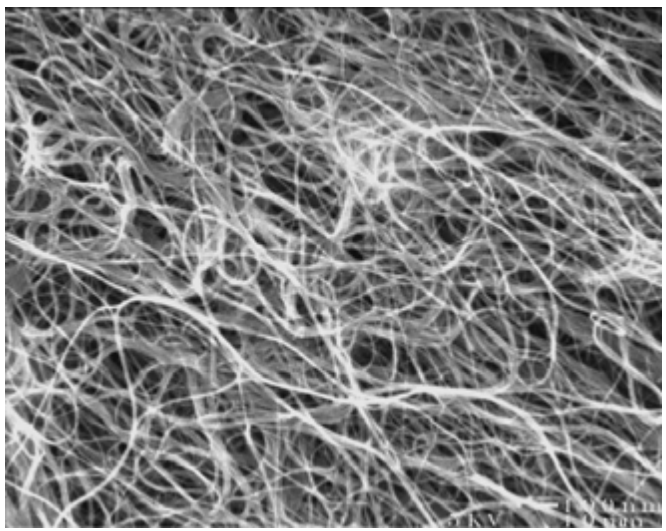
From analysis of H-SWNT interaction, move to a large scale molecular dynamics simulations, as shown, including thermodynamic-integration for computing thermodynamic potentials of the joint SWNT-array-hydrogen systems, as storage battery prototypes.

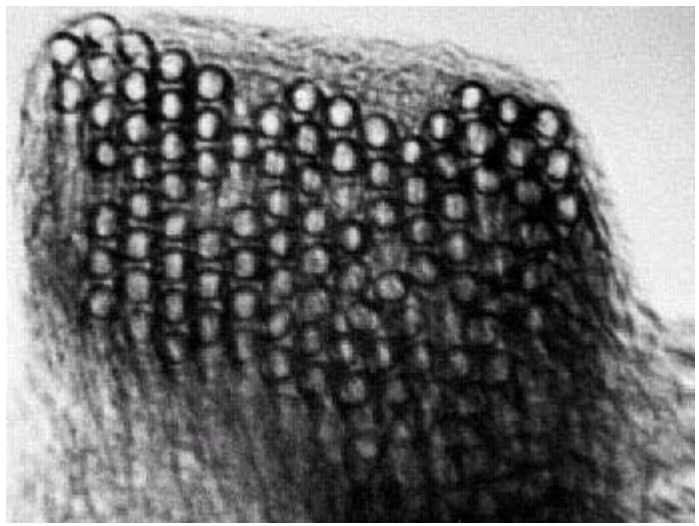
Besides thermodynamics of H-binding, we will investigate kinetics of hydrogen redistribution along the SWNT surface. Quantum computations of the activation barriers for H-hopping will be input into and transition state theory in order to evaluate time-scale of storage cycle and the necessity of metal catalyst spillover.



Why SWNT?

- The Scale and Perfection of DNA
- The Strongest Possible Fiber
- Thermal Conductivity of Diamond
- The Unique Chemistry of Carbon
- Maximum Possible Surface Area
- Selectable Electrical Properties
  - Metallics Better Than Copper
  - Semiconductors Better Than InSb or GaAs
- *The Ultimate Engineering Material*



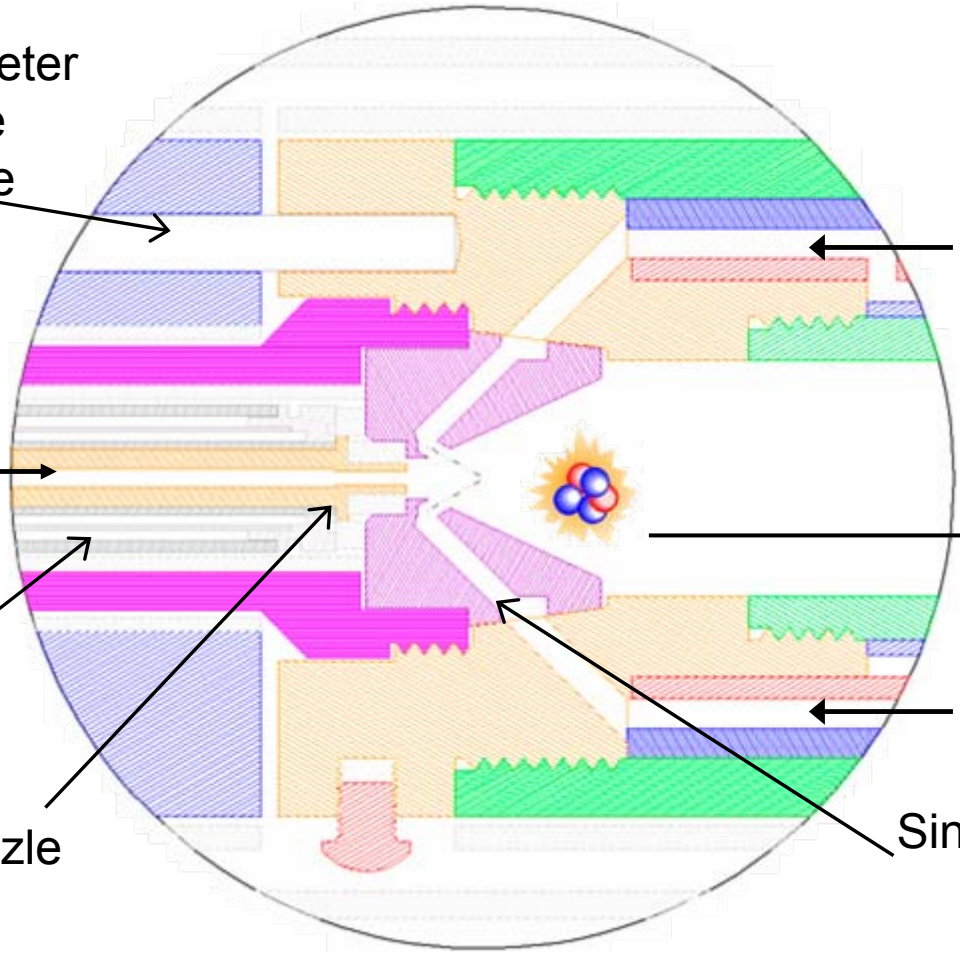


The HiPco Process

- High Pressure CO (HiPco) at ~1000 ^{o}C is mixed with room temperature gas containing gas phase iron pentacarbonyl
- Standard operating conditions are iron carbonyl at 52 mtorr in the reactor with an overall reactor pressure of 30 atm
- The iron nucleates forming small iron clusters a few atoms in size
- These iron clusters then catalyze the Boudouard reaction
- $2\ CO \rightarrow CO_2\ (g) + C\ (s)$
- Nucleated catalyst particles grow SWNTs
- The SWNTs are filtered out and the CO is recycled to create a continuous process

HiPco Reactor

HiPco Mixing Zone



Optical Pyrometer to measure temperature

Hot CO

Cooled $Fe(CO)_5$ in CO

SWNT Creation Zone

Water-cooled Injector

Hot CO

Copper Nozzle

Single-piece Graphite Showerhead

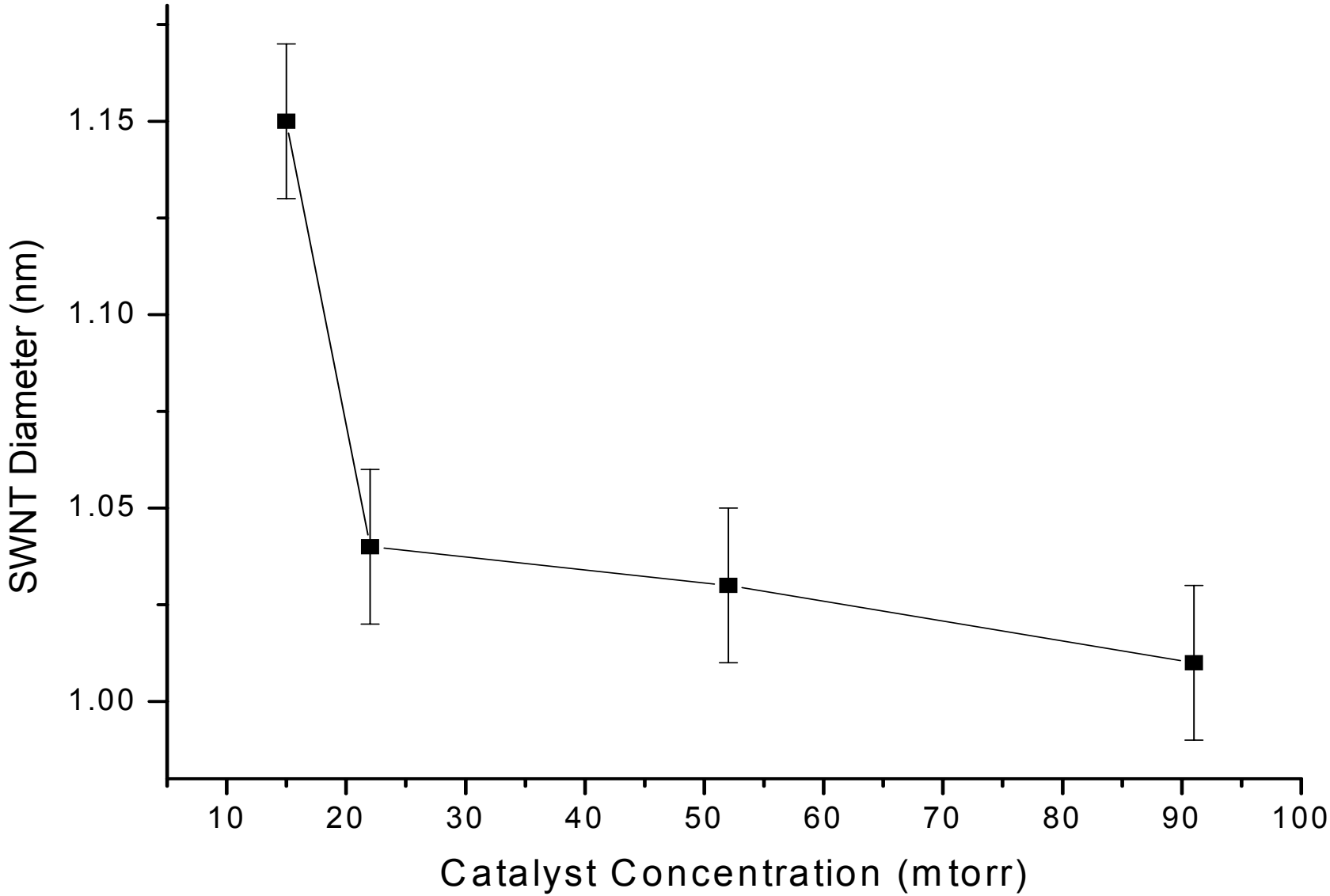
Single Wall Carbon Nanotube Production

This project aims to advance HiPco™ production in order to enable a strong material-supply base for hydrogen storage.

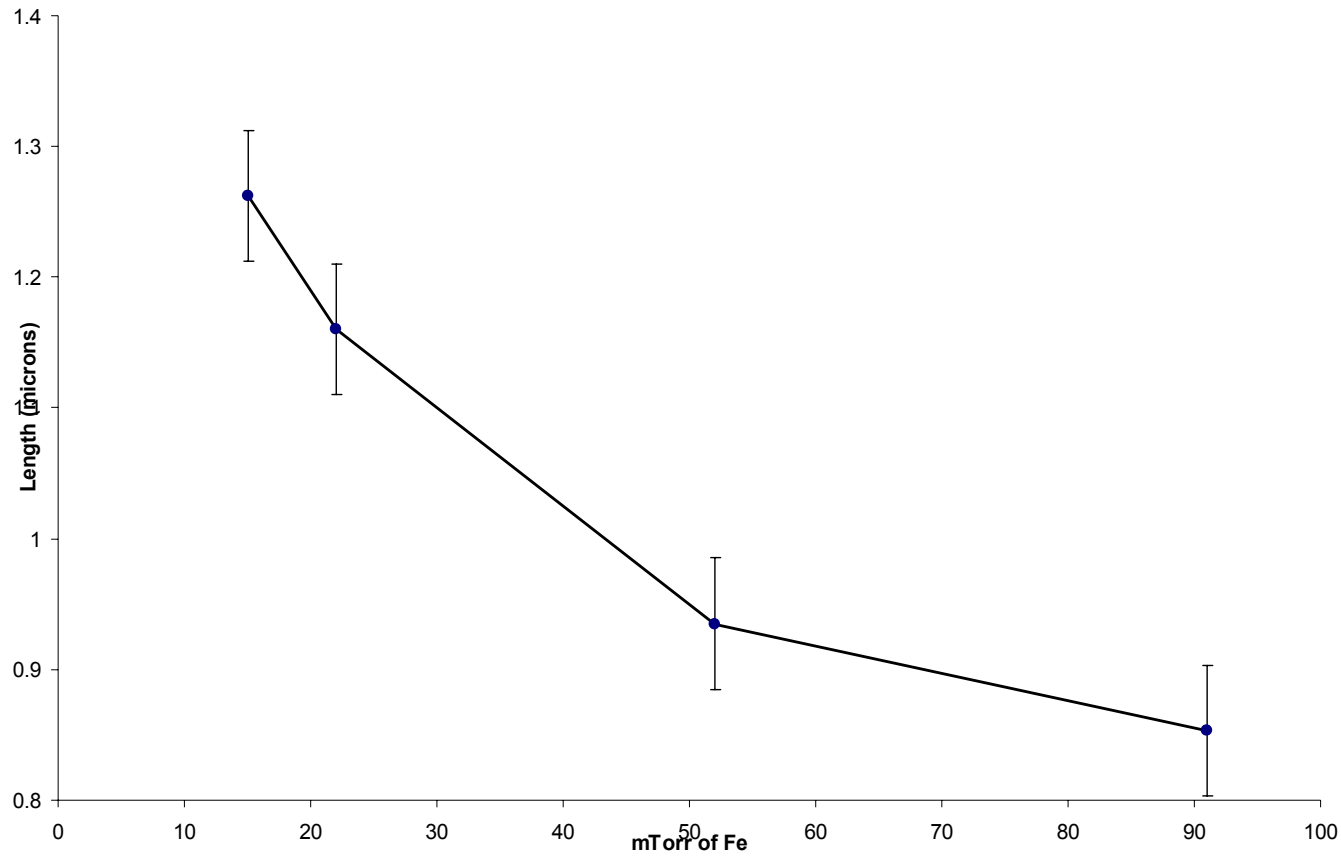
We will take advantage of tunability of HiPco™ and guide the production conditions based on detailed theoretical models of $\mathbf{H_2}$-swnt interactions and their possible enhancement

Effects of Metal Catalyst Concentration Variation On Single Wall Carbon Nanotube Properties In the HiPco Reactor

Average SWNT Diameters



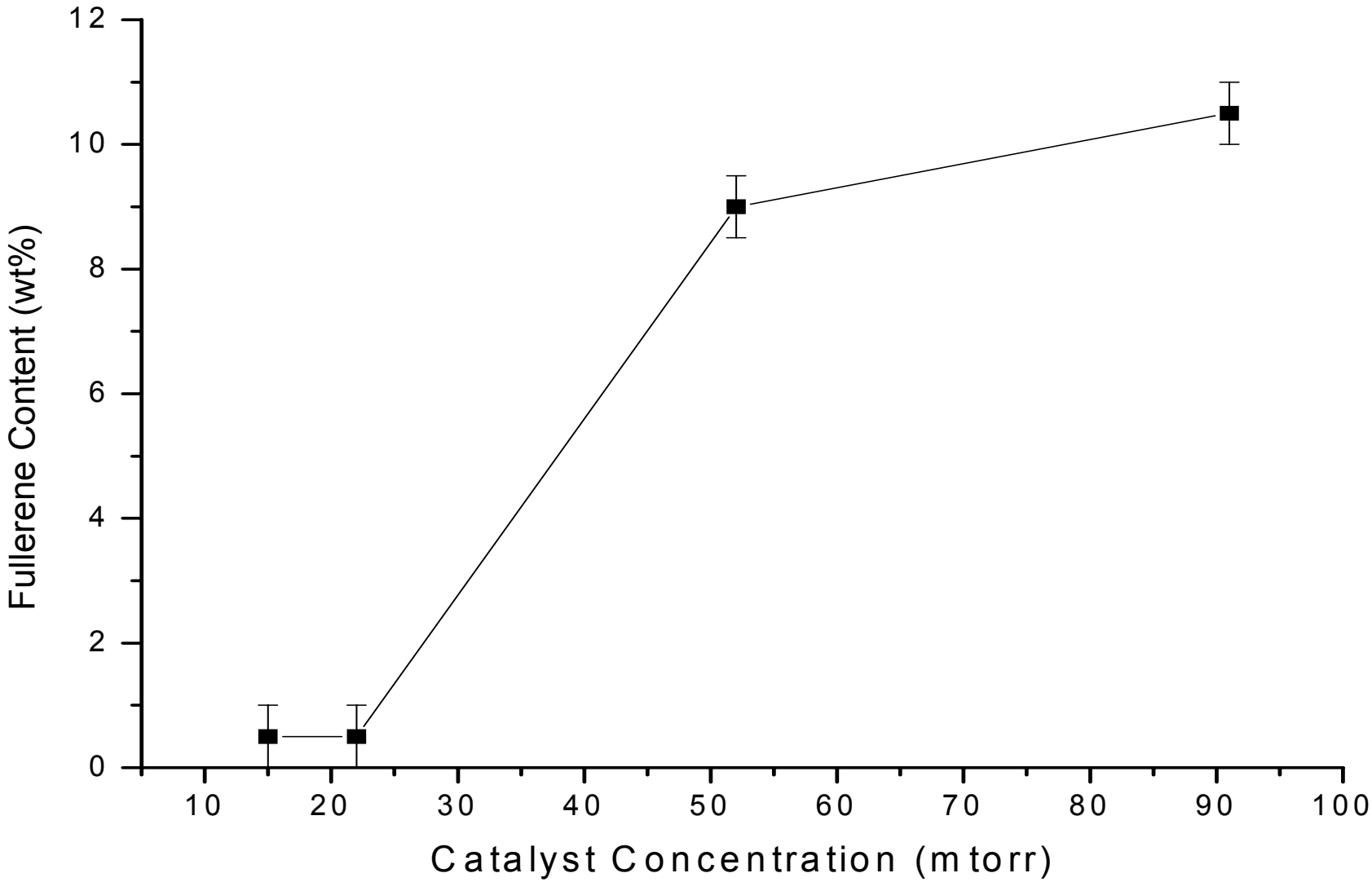
Average SWNT Lengths



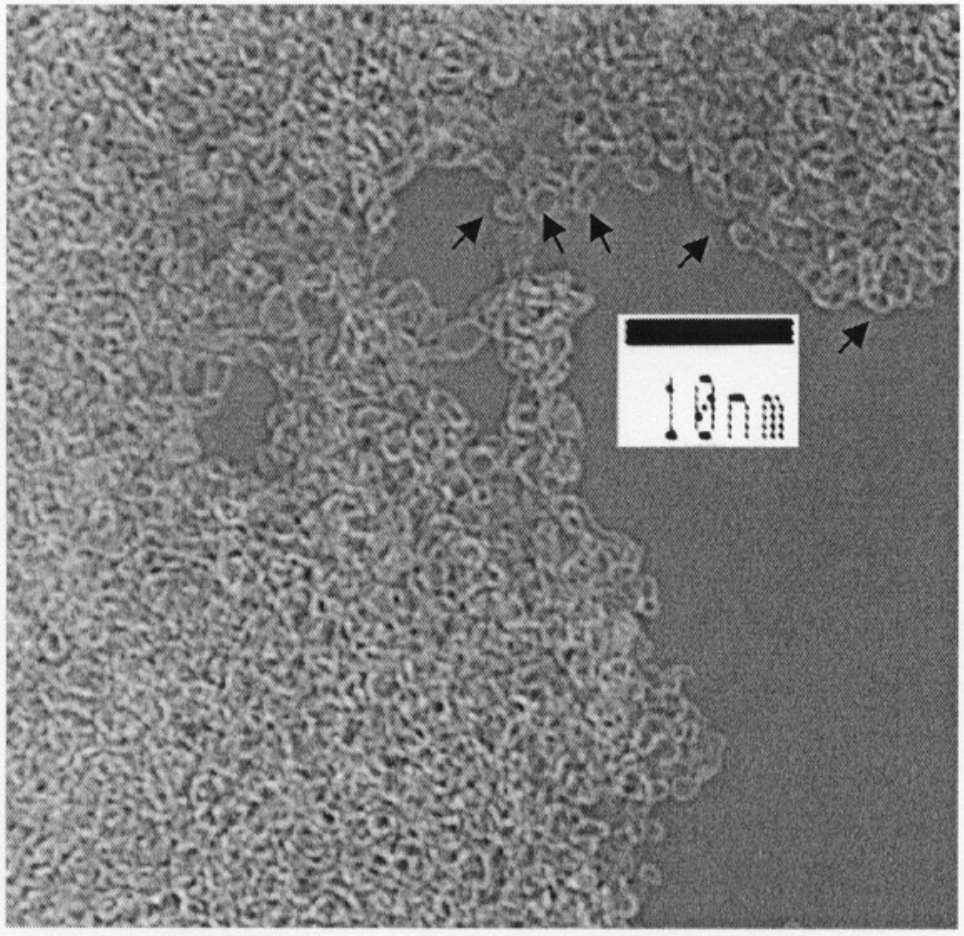
Superfullerenes

Superfullerenes, the end caps of single wall carbon nanotubes joined together, will be studied as a subset of swnt and in combination with swnt as high surface area supports for molecular hydrogen adsorption.

Large Fullerene Production



Large Fullerenes



- Large fullerenes extracted from raw HiPco Sample by fluorination

Milestones, Interactions & Safety

- **Milestones (fy05)**
  - Compute binding energies & saturation limit for various SWNT types
  - Compute quantitative maps of H binding energies afa tube radius
  - Estimate H hopping barriers along SWNT
  - Production of 50 grams of HiPco material optimized for H2 adsorption
- **Milestones (fy06)**
  - Compute binding energies & saturation limit for various SWNT types
  - Compute quantitative maps of H binding energies afa tube radius
  - Estimate H hopping barriers along SWNT
  - Production of 50 grams of HiPco material optimized for H2 adsorption
- **Interactions**
  - Smalley & Heben on SWNT Growth
  - Modelers on Hydrogen Storage Team (
- **Safety**
  - No lab safety or materials issues expected
- **Go/no-go decision**
  - Go/no-go decision of the use of swnt as hydrogen storage material at the end of fy06

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- New Start

Barriers

Reversible Solid-State Material Storage Systems:

Hydrogen Capacity and Reversibility

Lack of Understanding of Physisorption and Chemisorption *variability*

Test Protocols and Evaluation Facilities

Budget

- **Expected Total Funding**
- **Total $1,072,515**
  - **DOE share $857,996**
  - **Contractor share $214,520**
- **Funding for FY05 $200,004**

Partners

- Interactions - NREL, Air Products
- Collaborations - Duke Univ.,ORNL