Synthesis of Small Diameter Carbon Nanotubes and Microporous Carbon Materials for Hydrogen Storage

-Carried in the "Hydrogen Sorption Center of Excellence "

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Project ID # STP4

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent Complete: 40%

Budget

- Expected Total Funding
  - DOE share: $500,000
  - Contractor share: $125,000
- Funding for FY06
  - DOE Share: $100,000
  - Contractor share: $25,000
- Funding for FY07
  - DOE Share: $100,000
  - Contractor share: $25,000

Barriers and Targets

- Barriers addressed

  A. Cost.

  B. Weight and Volume.

  C. Efficiency.

  M. Hydrogen Capacity and Reversibility.
- Targets

  System Gravimetric capacity: >6%

  Volumetric capacity: >0.045 kg/L

Partners

- Interactions/ collaborations
  - NREL
  - UNC
  - Oak Ridge National Lab
  - Rice University
  - University of Georgia

Objectives of Research

- Overall:
  - Design and synthesize carbon based materials with optimized binding energy to hydrogen molecules that will show storage capacity meeting DOE year 10 goal in hydrogen storage.
    - Small Diameter Carbon nanotubes (Phase I)
    - Uniform Microporous Carbon Materials with Small Pore Sizes (Phase I and II)
- Phase I (FY05-FY06):
  - Validate theoretical prediction that small diameter single walled carbon nanotubes have enhanced binding energy to hydrogen molecules;
  - Develop method to synthesize gram quantity small diameter single walled carbon nanotubes.
- Phase II: (FY07-FY09):
  - Complete evaluation of small diameter carbon nanotubes;
  - Design and synthesize microporous carbon based materials with enhanced binding energy to hydrogen:
    - Pore size control;
    - Metal doping of microporous carbon materials;
    - B doping of microporous carbon materials.

Approaches

Small Diameter Single Walled Carbon nanotubes:

- Synthesize single walled carbon nanotubes with diameter smaller then 1 nm using chemical vapor deposition method;
- Achieve the control of nanotube diameter through understanding of the effect of growth conditions, such as catalysts and carbon feeding rate, on the diameter of carbon nanotubes;
- Measure the storage capacity of small diameter carbon nanotubes and compare with nanotubes samples with larger diameters to validate theoretical prediction;
- Prepare carbon nanotubes with metal decoration to study the "spill-over" mechanism for hydrogen storage.

Microporous Carbon Based Materials:

- Using organic template and solution synthesis method to prepare porous carbon materials with average pore size smaller than 1 nm;
- Collaborate with theoretical groups to establish models that can predict the effect of pore sizes on hydrogen storage capacity;
- Incorporate dopants into precursors for the preparation of metal doped microporous carbon materials and Boron-doped microporous carbon materials.

Technical Accomplishments

- Developed understanding on the relation between the carbon feeding rate and the diameter of prepared nanotubes (in FY05-06). Identified conditions under which small diameter CNTs can be prepared;
- Prepared small diameter carbon nanotubes in bulk quantity for measurements;
- Characterized the storage capacity of various carbon nanotubes at 77 K and 2 bar at NREL;
- Identified major technical problems associated with the preparation of large quantity carbon nanotubes with small diameters;
- Prepared high purity double walled carbon nanotubes for testing of their hydrogen storage properties;
- Developed methods to prepare microporous carbon materials;
- Developed methods to decorate CNTs and microporous carbon materials with small metal nanoparticles for the study of their effect on hydrogen storage properties.

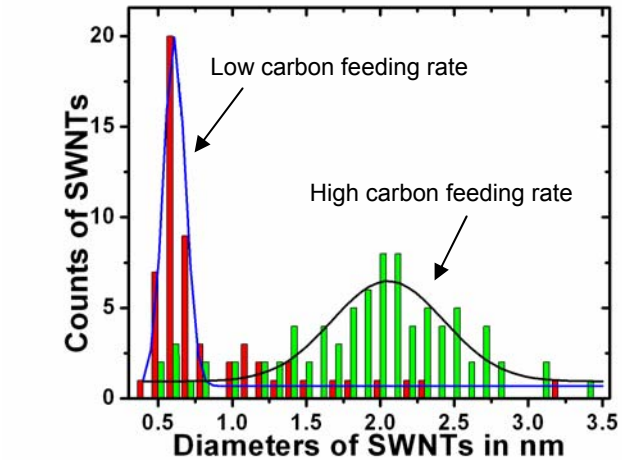
Demonstrated Control of CNT Diameter through Carbon Feeding Rate Variation

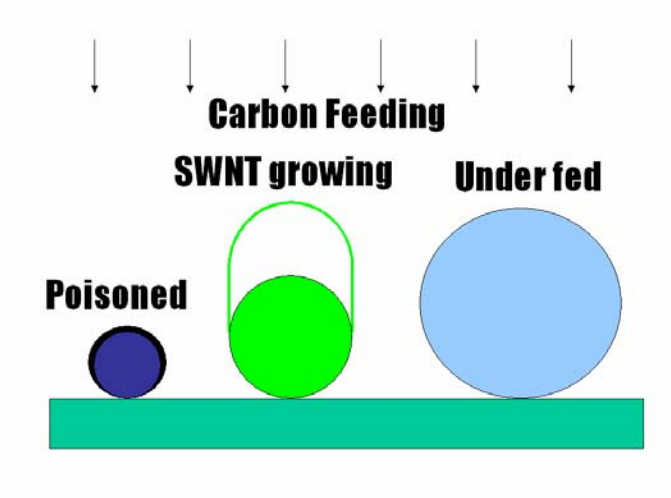
(From last year's Review)

Progress:

- Discovered that the size of CNTs are closely related to the growth conditions, most importantly carbon feeding rates.
- Discovered that uniform small diameter CNTs can be produced from non-uniform catalysts if the growth conditions are controlled precisely.

Diameter distributions of CNTs grown 800°C.





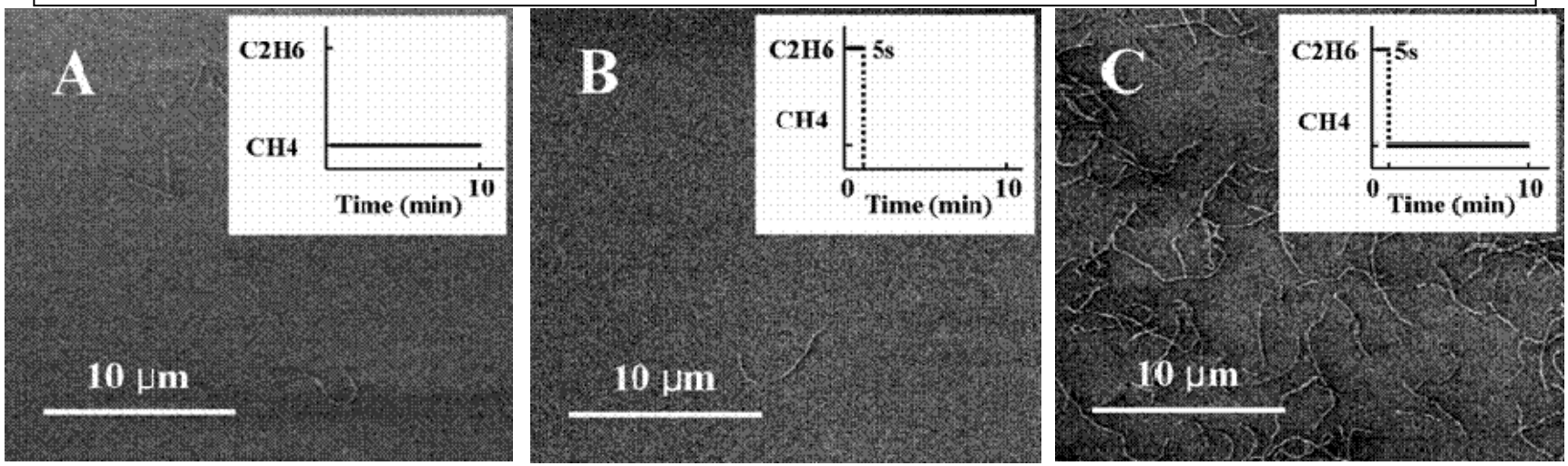
Mechanism:

1. At a given set of growth conditions, there exist an optimum size for catalyst nanoparticles to nucleate CNTs;
2. Too big or too small catalysts can not nucleate CNTs efficiently;
3. Slow carbon feeding rate favor the growth of small diameter nanotube

Demonstrated the Importance of Growth Conditions at Nucleation Stage on the Yield and Diameter of Carbon Nanotubes

Progress:

- Discovered that the growth of CNT in a chemical vapor deposition process can be separated into nucleation stage and continued growth stage;
- The optimized conditions for the two stages are different.
- When high carbon feeding rates are used for the nucleation stage and low carbon feeding rates are used for the growth stage, the yield of carbon nanotube is highest;
- The diameter of carbon nanotubes is closely related to the conditions used for both stages.

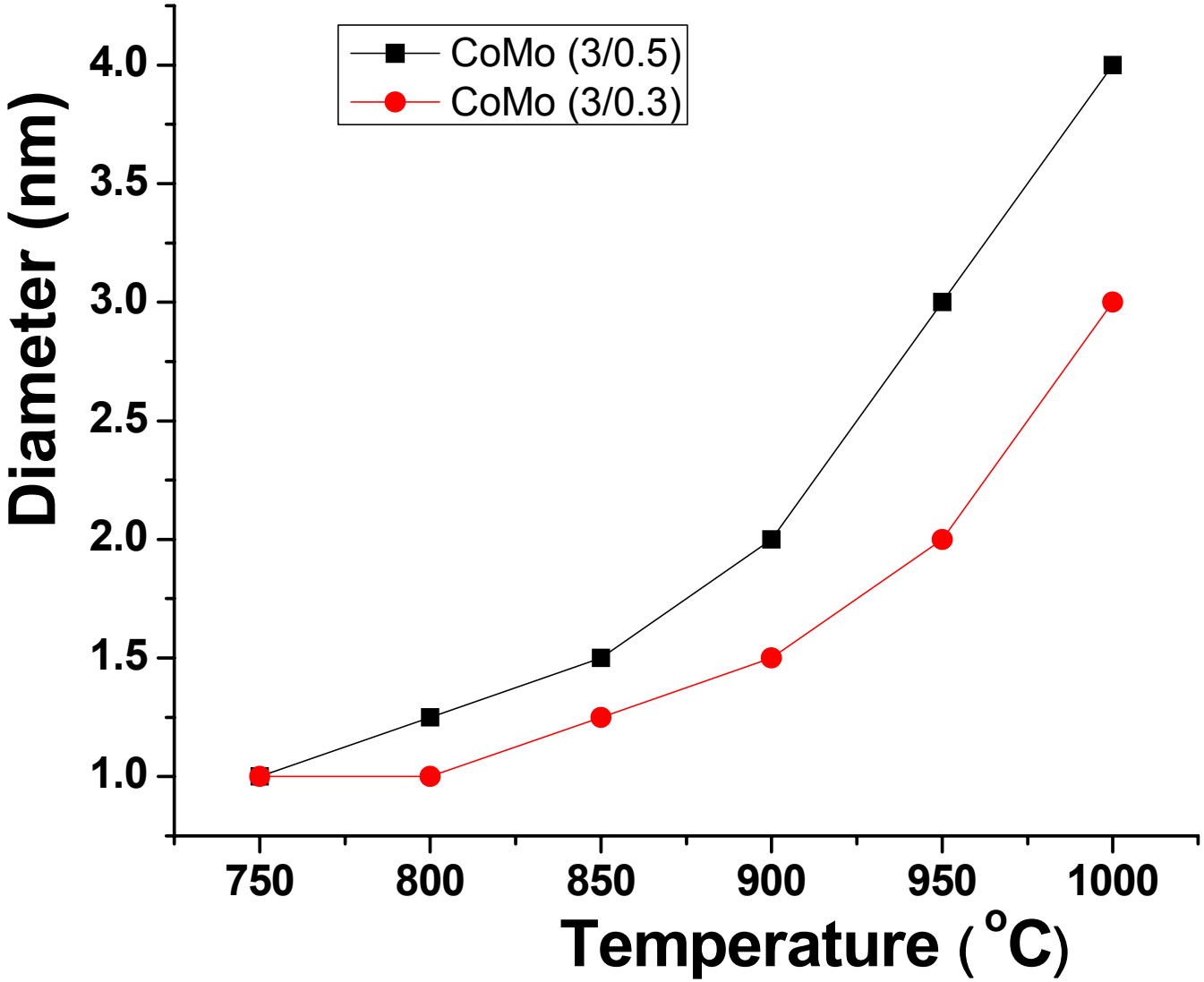


Demonstrated the Effect of Growth Temperature on the Diameter of CNT in Bulk Synthesis----I

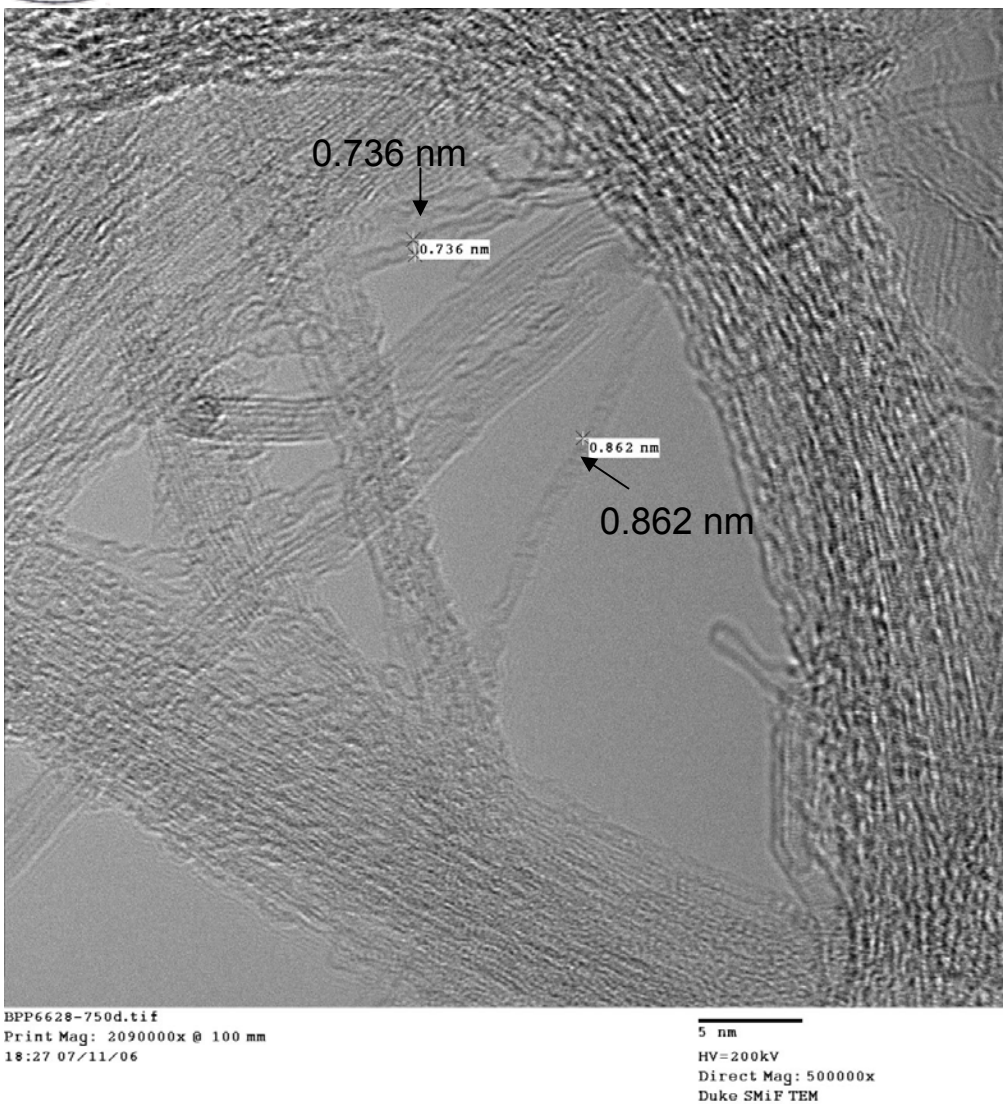
Catalyst composition	CoMo/MgO (3/0.5/200)	CoMo/MgO (3/0.3/200)
750 °C	SWNTs, less than 1nm in diameter	SWNTs, less than 1nm in diameter
800 °C	Mixture of SWNTs & DWNTs with 1-1.5nm average diameter	Mixture SWNTs & DWNTs with about 0.8-1.5nm in diameter
850 °C	Mixture of DWNTs & SWNTs with more DWNTs, diameter around 1.5nm	Mixture of SWNTs & DWNTs with more SWNTs, diameter about 1-2nm
900 °C	Mixture of DWNTs and TWNTs, diameter between 2-3nm	Mixture of DWNTs and SWNTs with more DWNTs, diameter between 1-2nm
950 °C	FWNTs, mostly DWNTs and TWNTs, diameter between 2-3nm.	DWNTs, diameter between 1.5-3nm.
1000 °C	FWNTs, mostly three and four walls CNTs, diameter around 4nm.	Mostly DWNTs, with some TWNTs, diameter between 2~4nm.

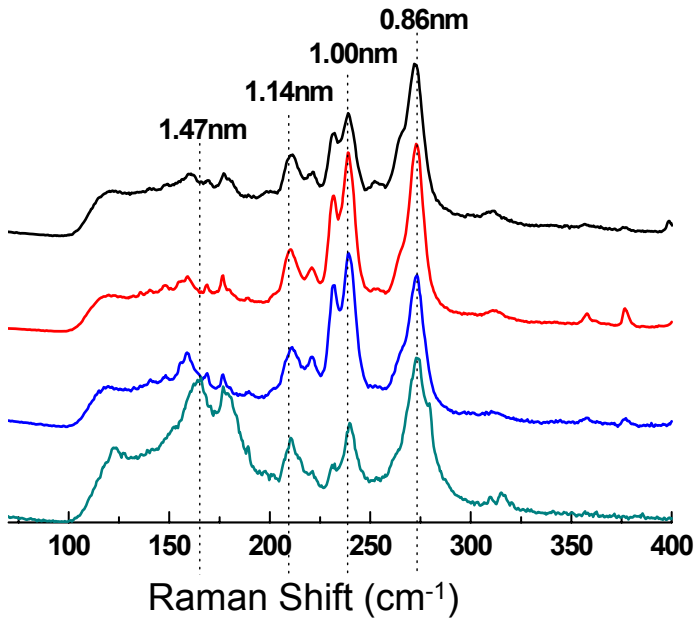
SWNT; Single Walled carbon nanotubes
DWNT: Double walled carbon nanotubes
TWNT: Triple walled carbon nanotubes
FWNT: Few walled nanotubes, mostly 3-4 walls

Demonstrated the Effect of Growth Temperature on the diameter of CNT in Bulk Synthesis----II



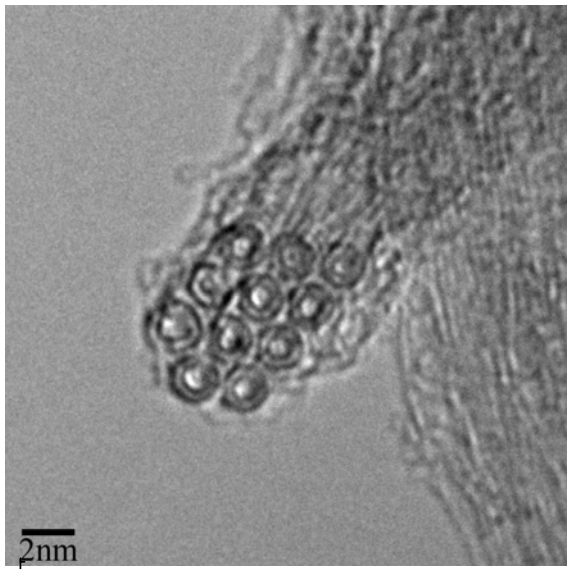
Prepared Bulk Quantity of Nanotubes with Average Diameters Smaller than 1 nm

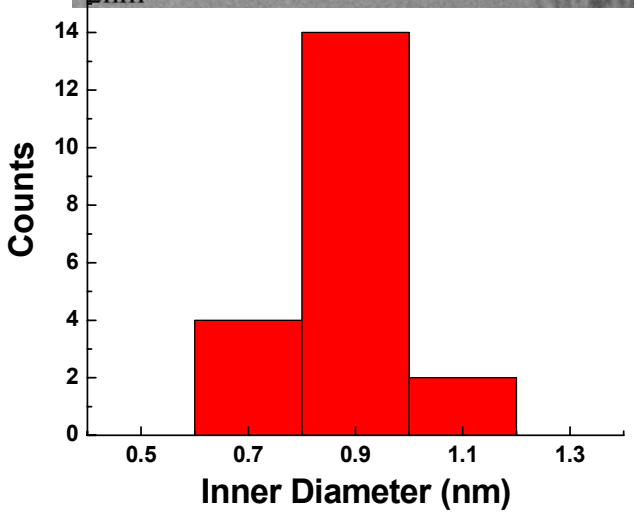


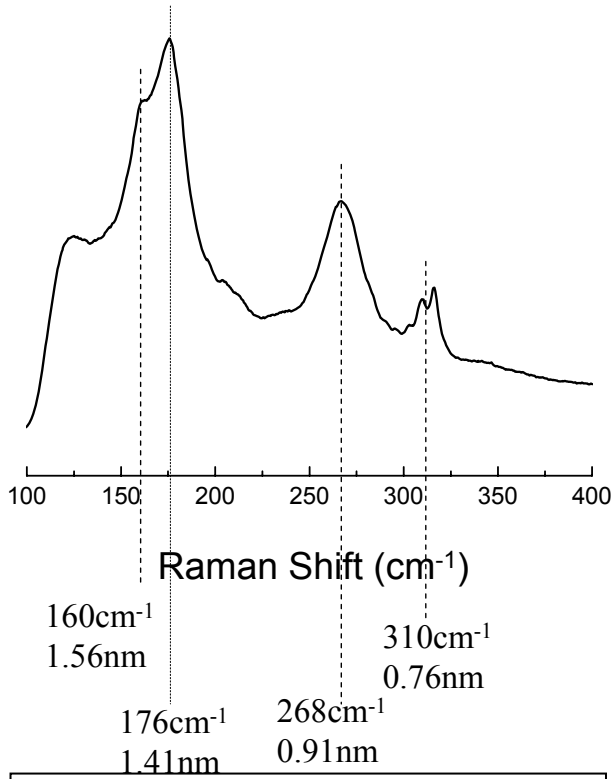


TEM and RAMAN data of bulk quantity nanotubes with average diameters less than 1 nm. Different curves in Raman data are from samples made at different growth conditions.

Prepared Bulk Quantity of Double Walled Carbon Nanotubes







HR-TEM Image, Diameter distribution from TEM data and RAMAN of bulk quantity double walled carbon nanotubes

Samples prepared to validate a recent claim that DWNTs are better candidates for hydrogen storage: *Miyamoto, et al., JACS 128, 12636 (2006)*

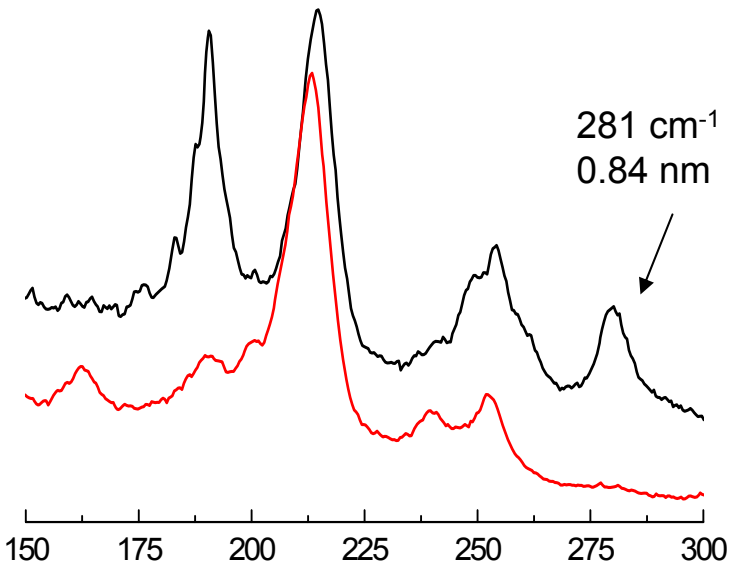
Compared Hydrogen Storage Properties of Small Diameter SWNTs, DWNTs and SWNTs with Larger Diameters—Measurements Performed at NREL

Table 1. Summary of measurements on small diameter SWNT and DWNT materials

Measurement	0.9 nm SWNT	1-2 nm SWNT/DWNT	0.9 nm SWNT + 2 nm Pd	1-2 nm DWNT	Small d Commercial SWNT	Typical NREL SWNT
Sieverts RT & 2 bar as received	0.007 wt%	0.011 wt%	0.36 wt%		0.04 wt%	
Sieverts 77 K & 2 bar as received	0.39 wt%	0.54 wt%	0.58 wt%	0.04 wt%	1.13 wt%	
BET SA as received	350 m^2/g	420 m^2/g	269 m^2/g	42 m^2/g		
Modified Chahine Criterion (wt% per 500 m^2/gm)	0.56	0.64	1.08	0.48		
TPD: 500 torr dose at RT cooled to 77K as received			0.39 wt% total ~0.24 wt% Pd, ~0.15 wt% Chemi.			
Sieverts 77 K & 2 bar after 800 °C degas				0.11 wt%	1.43 wt%	
BET SA after 800 °C degas				82 m^2/g	880 m^2/g	
Sieverts 77 K & 2 bar after 800 °C					1.61 wt%	
BET SA after 800 °C CO2				75 m^2/g	1074 m^2/g	
Sieverts 77 K & 2 bar after H_2SO_4 reflux, CO_2 to 700 °C, HCL soak, CO_2 to 700 °C		0.84 wt%				1.7 wt%
BET after H_2SO_4 reflux, CO_2 to 700 °C, HCL soak, CO_2 to 700 °C		630 m^2/g				630 m^2/g
Modified Chahine Criterion (wt% per 500 m^2/gm)		0.67		0.67	0.75	1.35

- No improved storage capacity in small diameter SWNTs was observed;
- Surfaces may be inaccessible due to impurities or adsorbed acid species.

Identified a Major Challenge Related to the Purification of Small Diameter SWNTs



RAMAN data of small diameter SWNTs. Black curve is for raw samples and red curve is for samples purified in air at 350ºC

- Both TEM and Raman studies showed the disappearance of small diameter SWNTs after purification process;
- Small diameter SWNTs are more reactive towards the oxidizing environment used for purification and thus destroyed during the purification process;
- This could be a major practical problem for applications like hydrogen storage using small diameter SWNTs;
- Purified nanotubes with average diameter < 1nm were obtained by lower temperature (300ºC) oxidation. However, other purification methods that can remove impurities, mostly amorphous carbons, need to be developed without the use of oxidizing environment. A possible solution is the use of ultra centrifuge to remove impurities from nanotubes.

Developed Methods to Synthesize Microporous Carbon Materials Using Organic Templates--I

Motivations

- Microporous carbon materials, such as CDC (carbide derived carbon) and Zeolite-templated carbon have demonstrated good hydrogen storage capacities (up to 3 wt% at 77K and 1 bar; 6.9 wt% at 77K and 20 bar)[1-2].
- Organic-templated porous carbon offers unique advantages compared to CDC and Zeolite-templated carbon, including the control of pore size, the flexibility in adding various dopants, the low cost in large scale synthesis and the elimination of highly toxic chemicals like chlorine and HF.
- Such materials offer a way to systematically study the effect of pore size, metal doping and B doping on the binding energy to hydrogen molecules. The ability to tune these parameters in the materials makes the design and synthesis of an ideal hydrogen storage media a possibility.

Approach

- Using various surfactant molecules to form micelles in a solution. Different surfactants will form micelles with different sizes;
- Introduce a polymerizable precursor into the solution that will interact with the outer surface of the micelles;
- Trigger the polymerization reaction to form a strong framework of polymers using micelles as templates;
- Thermally remove the surfactants;
- Graphitize the polymer at high temperature to form desired materials.

(1) G. Yushin, R. Dash,J.Jagiello, J.E.Fischer and Y.Gogotsi, Advanced Functional Materials, 16, 2288-2293 (2006).
(2)Z. Yang,Y. Xia,and R. Mokaya, JACS, 129, 1673-1679 (2007)

Developed Methods to Synthesize Microporous Carbon Materials Using Organic Templates--II

Challenges and Solutions

- **Pore size control:** The pore size control is an important issue in making a suitable material for hydrogen storage. It has been shown that the storage capacity is closely linked to the surface area related to *microporosity*. To achieve pore size control, different surfactant/co-surfactant will be used as templates and the controlled shrinkage during the removal of templates will also be carefully studies by changing the annealing temperature and environment.
- **Doping:** Pure microporous carbon materials already demonstrated 3 wt% storage at 77K and 1 atm, 6.9 wt% at 77K and 20 bar.[1-2] However, to improve the storage capacity to the DOE Year 10 goal of 6 wt% (including the weight of the whole system) with appropriate adsorption and desorption temperature, doping with metal and/or boron is a necessary step. Polymerizable precursors with metal atoms and Boron atoms will be used to introduce the desired concentration of dopants in this system.
- **Binding Energy with Hydrogen:** The key assumption of the research project is that the binding energy to hydrogen can be controlled to be higher than physisorption and lower than covalent bonding. Too low a binding energy results in low storage capacity and too high a binding energy causes problem in heat management. Through the control of pore size and doping concentration, it is highly possible that we can tune the binding energy continuously to obtain materials with optimized binding to Hydrogen.

(1) G. Yushin, R. Dash,J.Jagiello, J.E.Fischer and Y.Gogotsi, Advanced Functional Materials, 16, 2288-2293 (2006).
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Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY06 materials****	**FY07 Result**
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)	0.6 wt%*, (2 bar, 77K)	0.84 wt%*, (2 bar, 77K)
Volumetric Energy Capacity)	kWh/L	1.5		
Desorption Temperature				
Plateau Pressure				

* Measurements were performed at 2 Bar pressure, higher pressure measurement up to 70 bar is scheduled for later this year.

Future Work

- **Pore size control in Microporous Carbon Materials**
  - Develop scalable method to synthesize microporous carbon materials using organic molecules as templates. Using different surfactant molecules and different annealing temperature to control pore size distribution of the materials.
  - Comparing with other approaches, such as CDC and Zeolite-templated carbon materials, the approach will offer more flexible control of pore size and doping concentration. It also avoids the use of highly toxic chemicals like Chlorine and HF.
- **Doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms**
  - Develop methods to use precursors containing metal atoms and Boron atoms to prepare microporous carbon with controlled doping.
  - Demonstrating the change of binding energy to hydrogen through doping. Do systematic study on the effect of pore size and doping level to discover the optimum binding energy for hydrogen.
  - Demonstrate the materials' storage capacity exceeds DOE system goal of 6% by weight.
  - Collaborating with B. Wang's group at University of Georgia in making B containing precursors for doping.
- **Theoretical Modeling of the Effect of Doping on Hydrogen Binding Energy:**
  - Collaboration with theory groups (Rice and Air product team) within the center to study the effect of doping on the binding energy to hydrogen and validate the prediction using experimental results.
- **Complete the Study on Metal Decorated Small Diameter Carbon Nanotubes and the Effect on Hydrogen Storage Properties (FY07)**
  - In collaboration with NREL, perform more systematic study on Pd decorated small diameter SWNTs to understand the effect of metal decoration on the binding energy to hydrogen.

On-Going and Expected Collaboration

- NREL
  - Characterization of nanotubes and microporous carbon samples for their structures and hydrogen storage properties.
  - Study the effect of doping of microporous carbon on the binding energy and hydrogen storage properties.
- UNC
  - Measurement of Hydrogen binding energy as a function of pore size, metal doping and boron doping in Professor Yue Wu's Lab.
- University of Georgia
  - Collaborating with Professor Binghe Wang's group in designing and synthesizing Boron containing precursors for synthesizing boron doped microporous carbon materials

Project Summary

Relevance:

- Understanding the effect of structure of carbon based materials on the binding energy to hydrogen and the storage capacity

Approach:

- Demonstrating that the small diameter/pore size of carbon based materials can increase the binding energy to hydrogen and improve the storage capacity.
- Controlling the diameter of SWNTs;
- Controlling the pore size and volume of mesoporous carbon materials using templates.
- Using metal and boron doping on carbon materials to improve storage capacity.

Technical Accomplishments:

- Developed understanding on the relation between the carbon feeding rate and the diameter of prepared nanotubes. Identified conditions under which small diameter CNTs can be prepared;
- Prepared small diameter carbon nanotubes in bulk quantity for measurements;
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- Developed methods to prepare microporous carbon materials;
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Proposed Future research:

- Pore size control in Microporous Carbon Materials
- Doping of the Porous Carbon Materials with Metal Atoms and Boron Atoms
- Theoretical Modeling of the Effect of Doping on Hydrogen Binding Energy:
- Complete the Study on Metal Decorated Small Diameter Carbon Nanotubes and the Effect on Hydrogen Storage Properties (FY07)

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