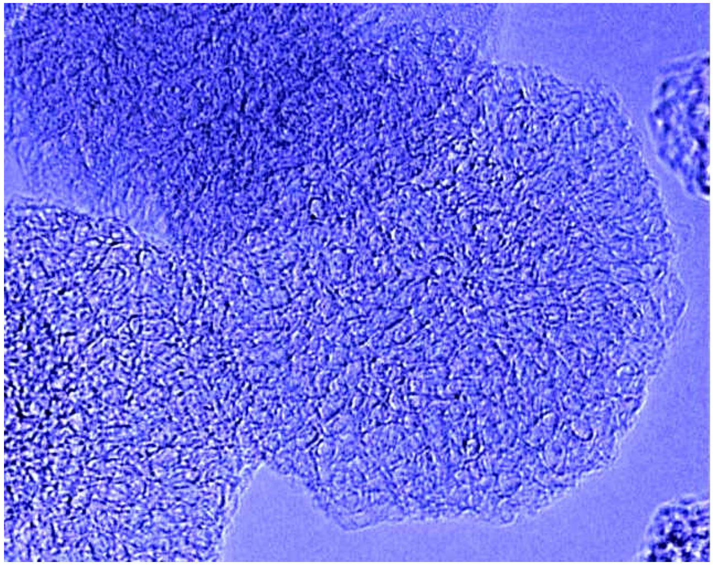
Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

David B. Geohegan, PI
Hui Hu
Alex Puretzky
Mina Yoon
Bin Zhao
Christopher M. Rouleau

Materials Science and Technology Division and the Center for Nanophase Materials Sciences
Oak Ridge National Laboratory, Oak Ridge, TN



Project ID STP-6

DOE Hydrogen Program Annual Review, May 15, 2007

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- 50% complete

Budget

- Total project funding
  - DOE share 1.9 M$
  - Contractor share 0k
- 300k received in FY06
- 300k for FY07

Barriers

- Barriers addressed
  - A. Weight and Volume
    - Reduced catalyst weight
  - B. Cost
    - Scalable production
  - C. Efficiency / Thermal Management
    - Composites
  - D. Durability / Operability
    - Catalyst stability
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
    - Catalyst-free production, tailorable pore sizes

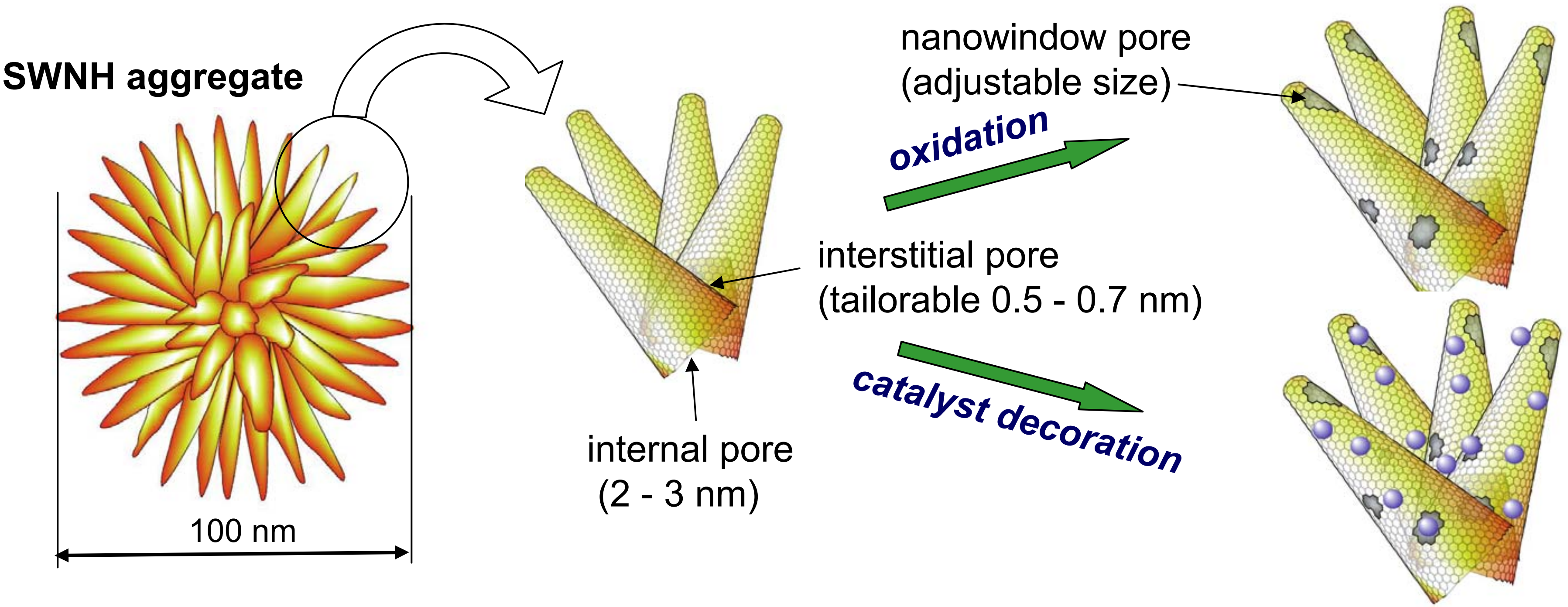
Partners

- Characterization: *(Partners)*
  - Hydrogen uptake - Air Products, NREL, NIST, CalTech
  - Neutron scattering - NIST
  - NMR - UNC
- Synthesis
  - Rice University
  - Duke University

Objectives

Overall	To control the synthesis and processing of a novel form of carbon – *single walled carbon nanohorns* – as a medium with tunable porosity for optimizing hydrogen storage
2006	A) Manufacture nanohorns in gram quantities by laser vaporization and control their morphology with *in situ* diagnostics. B) Develop chemical and thermal processing treatments to adjust and tune porosity of SWNHs, and methods to decorate them with metal clusters
2007	A) Coordinate synthesis and processing treatments to tune the surface area and porosity of SWNHs, and decorate them with metal clusters B) Vary pore size and metal decoration to work interactively with Center members to clarify the dominant mechanisms of hydrogen storage in metal-decorated nanohorns to address gravimetric and volumetric DOE targets ❍ Spillover ❍ Supercritical adsorption ❍ Dopant-induced charging

Nanohorns: Advantages Compared to Other Carbon Materials



- Single wall structures for maximal surface area, without bundling/dispersion problem.
- As synthesized, are excellent supports for metal nanoparticles.
- External and internal pore size can be adjusted and tuned by oxidation and pressing.
- Bottom-up approach (unlike CDC) with economical, pure material.
- Decorated by simple chemical procedures.
- Dense (1-1.5 g/cm^3) bulk material composed of nanohorns with uniform distribution of metal nanoparticles can be prepared (high expected volumetric capacities)
- Murata, et al. (J. Phys. Chem. B, 2002, 106, 11132), showed 70 g/L storage densities in both internal and external pores at 77K/ 5MPa.

Approach

Overall

Explore SWNHs as a tailorable nanoporous medium and metal cluster support for hydrogen storage

- Tune nanostructure during synthesis
- Tune nanoporosity and metal decoration of medium during processing

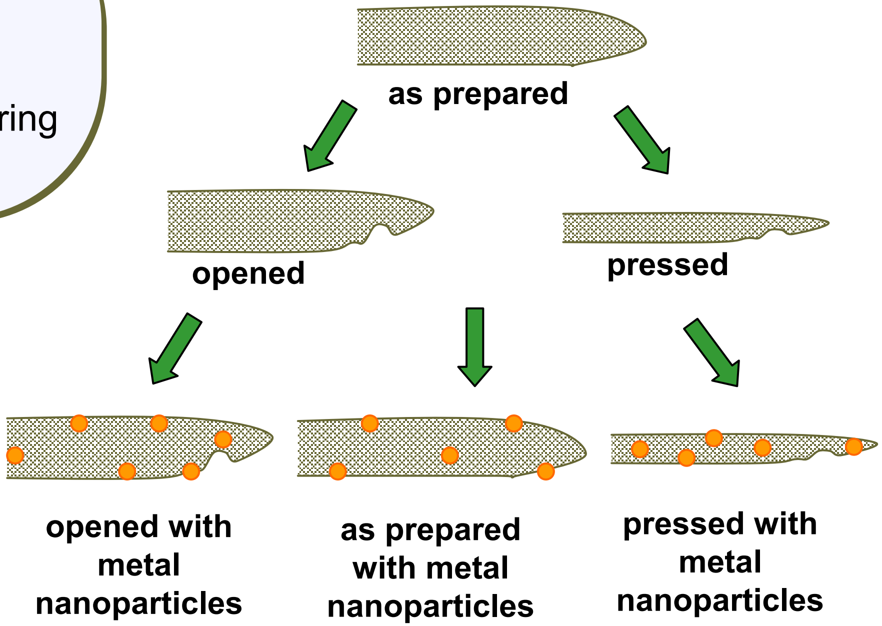
Synthesis & Processing

1. Control nanohorn unit and aggregate structures during synthesis, and produce grams quantities.
2. Develop nanohorn chemistry and processing treatments (heat, compression) to control pore size, surface area, and defects
3. Controllably decorate nanohorns with metal clusters for enhanced hydrogen storage

Hydrogen Storage

1. Understand dominant mechanisms for hydrogen adsorption in undecorated and decorated nanohorns through experiments (neutron scattering, NMR, TPD), nanostructural characterization (TEM, Raman, SEM, TGA), integrated theory, and modeling.
2. Adjust nanostructure and composition to meet DOE targets.

Different varieties of SWNHs



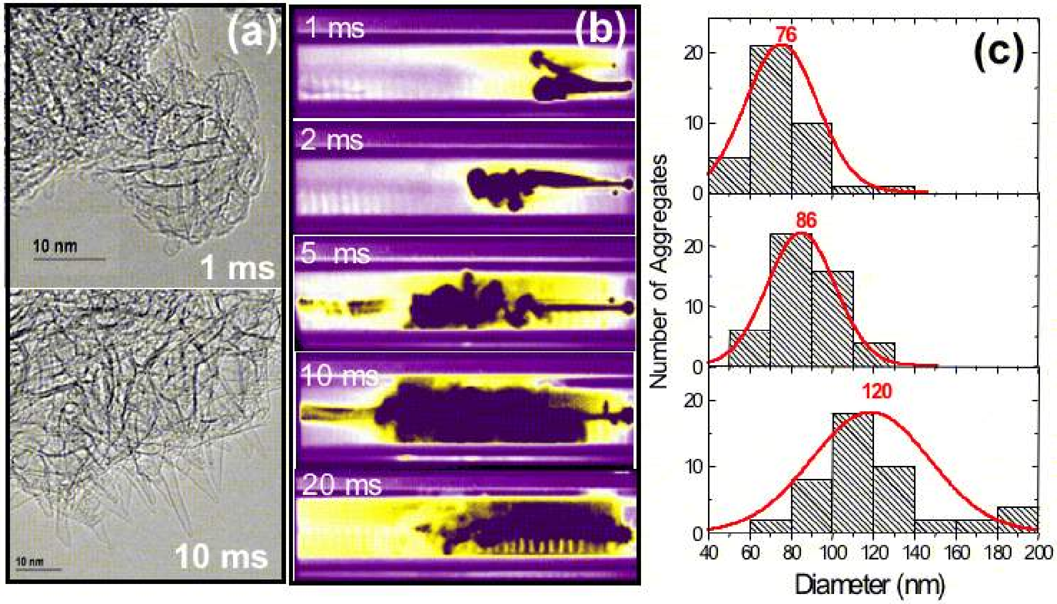
Summary of FY06 Results (by May 2006)

Synthesis:

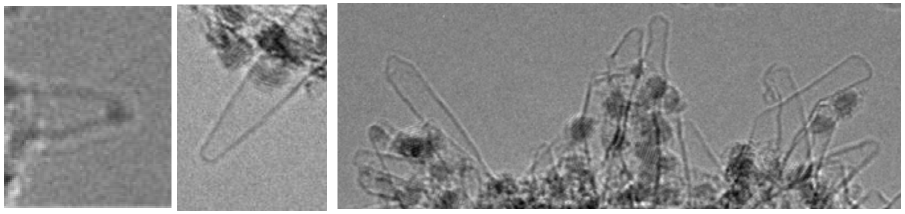
- Performed *in situ* diagnostics of nanohorn formation by laser vaporization.
- Demonstrated control of the aggregate size and nanostructure.
- Grams quantities of SWNHs were synthesized and delivered to partners.

Processing:

- Oxidation approaches were developed to open SWNHs to increase surface areas.
- Initial chemical methods were developed to decorate SWNHs with well-characterized Pt clusters (1-3 nm).
- Hundreds of milligrams of Pt-decorated and opened SWNHs provided to partners.



(a) TEM images of SWNHs produced at 1 ms and 10 ms of laser pulse width.
(b) Images of laser ablation plumes.
(c) Size distributions of SWNHs aggregates produced at different laser pulse widths



TEM images of metal decorated SWNHs

Adsorption:

- Initial hydrogen uptake, neutron scattering, and BET measurements were performed for 4 different classes of SWNHs by partners.

FY07 Technical Accomplishments / Progress / Results

- **Task 1: Controlled Synthesis of SWNHs with Varied Internal:External Pore Ratios by Laser Vaporization**
  - Single-wall carbon nanohorns (SWNHs) with tunable morphologies were synthesized at multigram scale at ORNL and delivered to participants, along with metal-decorated samples.

Milestone Achieved 3/07

Gram quantities of decorated nanohorns with well-characterized morphology delivered to partners

- **Task 2: Controlled Processing Chemistry - Tailor SWNH pore size, surface area, and metal decoration**
  - New methods of oxidative chemistry to produce high (1900 m^2/g) surface areas and variable pore sizes were developed.
  - Controllable deposition of Pt, Pd nanoparticles.
  - Compression and thermal treatments demonstrated to vary pore sizes and graphitic structure of SWNHs

Milestone Achieved 3/07

Thermal and oxidative treatments applied to vary pore size , surface area, morphology, and catalyst particle size to deliver well-characterized samples to partners for understanding dominant mechanisms of hydrogen storage

- **Results** (*with partners)*
  - Evidence for spillover mechanism in both Pt- and Pd-decorated SWNHs observed by neutron scattering monitoring of free H_2. Temperature onset for catalytic storage set between 150K < T < 298K. - (w/*NIST)*

Milestone in Progress 9/07

Assessment of dominant mechanisms responsible for hydrogen storage

  - Nuclear magnetic resonance observation of possible spillover-related room-temperature storage in Pt-decorated SWNHs,. *(w/UNC).*
  - Enhanced binding energies for Pt-decorated SWNHs measured by TPD (36 ± 2 kJ/mol, *NREL*) and NMR (7.1 kJ/mol, *UNC).*

Milestone in Progress 9/07

Adjustment of processing conditions based upon feedback from partners

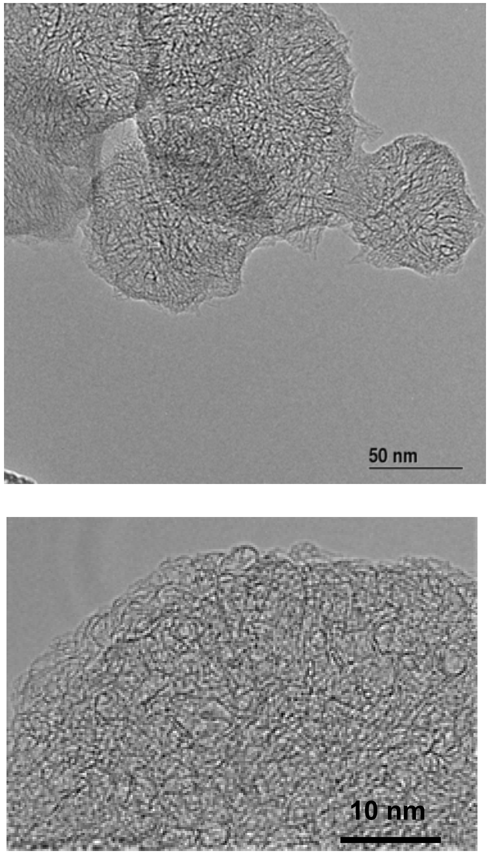
  - Hydrogen Storage *(w/CalTech, UNC, NIST, NREL)*
    - Room temperature results range from (0.2 - 0.8 wt.%)
    - 77K uptake (1 - 3.5 wt.%)
  - Theory and simulation of effects of metal decoration on hydrogen binding energy and storage: Prediction of enhanced binding energy vs. induced field strength.

NEW DIRECTION

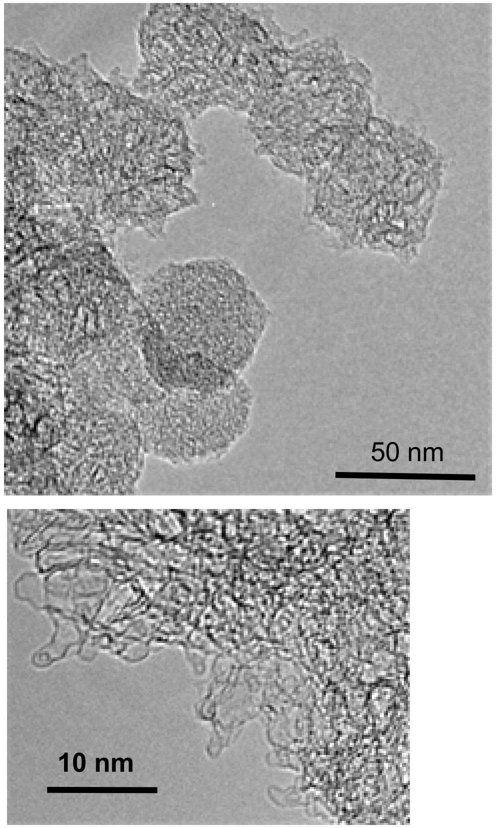
HYDROGEN STORAGE IN CHARGED NANOSTRUCTURES

Tuning Surface Area and Pore Sizes of SWNHs: Oxidative Processing in CO_2

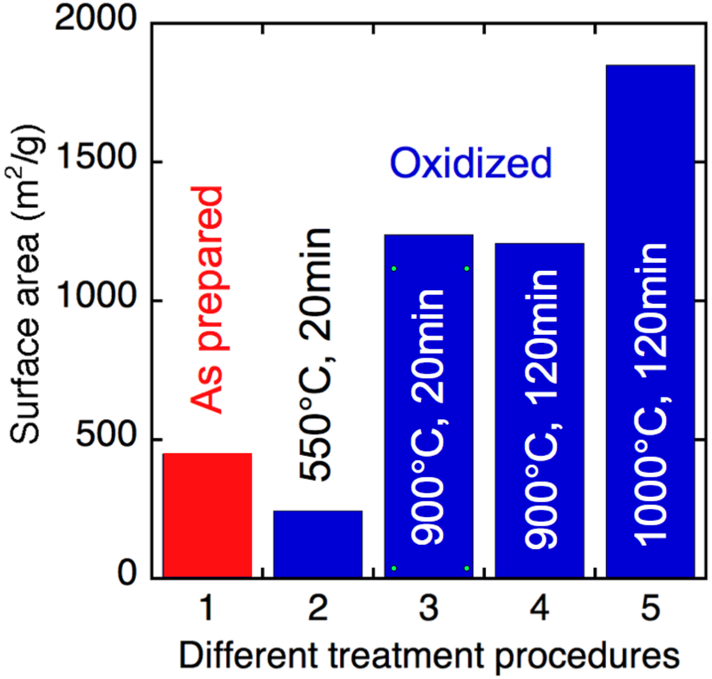
550°C/CO_2/20 min



900°C/CO_2/20 min



Surface area of SWNHs under different oxidations

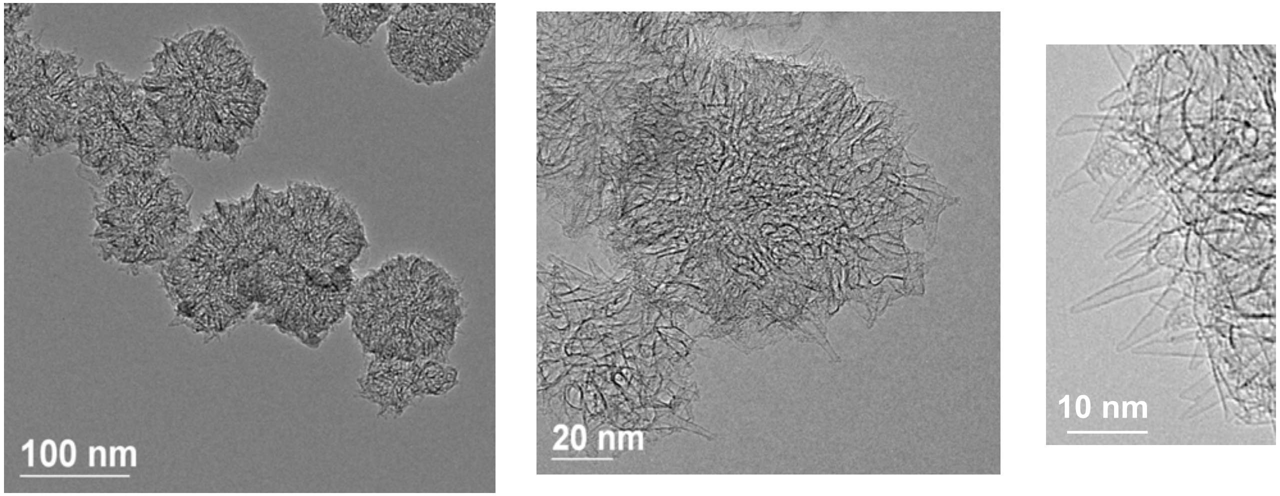


A new oxidation procedure of SWNHs in CO_2 was developed (more controllable than air oxidation), yielding a variety of new nanoporous pure carbons with different pore sizes and surface areas for optimal hydrogen storage.

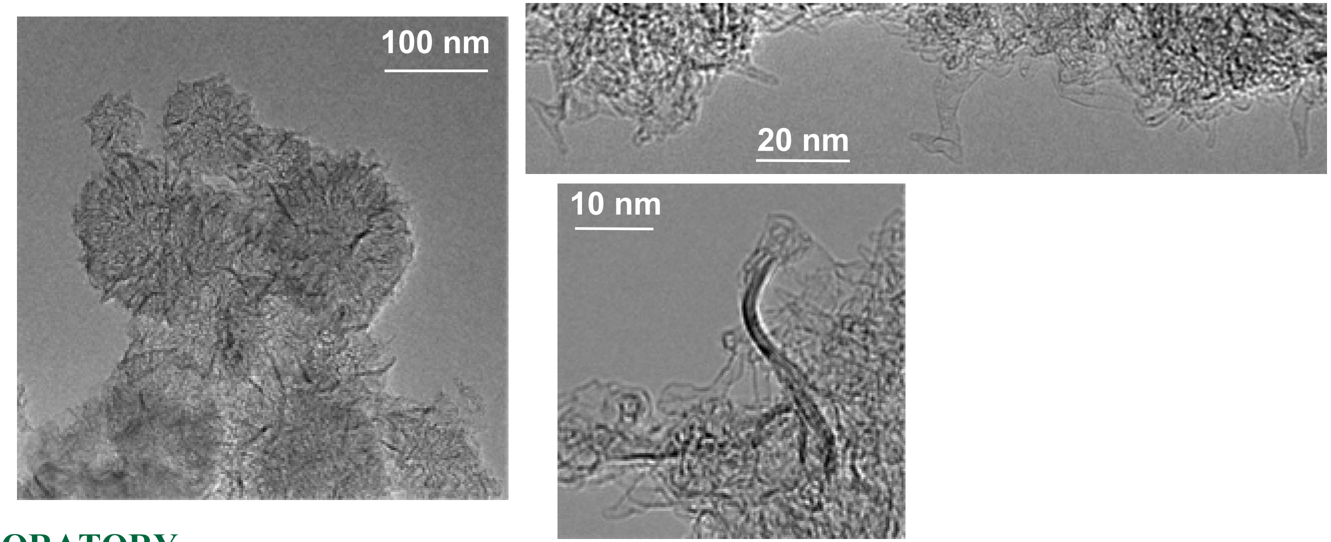
Compression and Annealing of SWNHs to Tune Structure and Address Volumetric Capacity

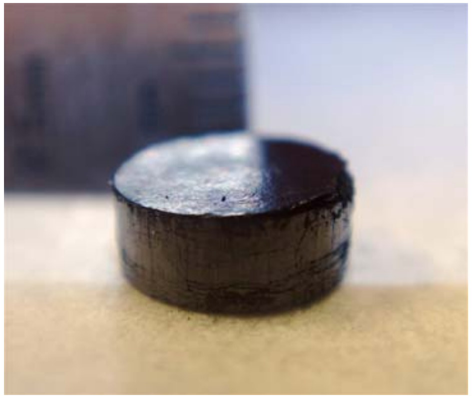
- *SWNHs can be compressed to form dense pellets (before annealing 1.03 g/cm^3)*
- *Pore sizes change*
- *Heat treatments change structure*
- *Volumetric density (assuming 3 wt. %) 31g/L*

As-prepared SWNHs before pressing and annealing



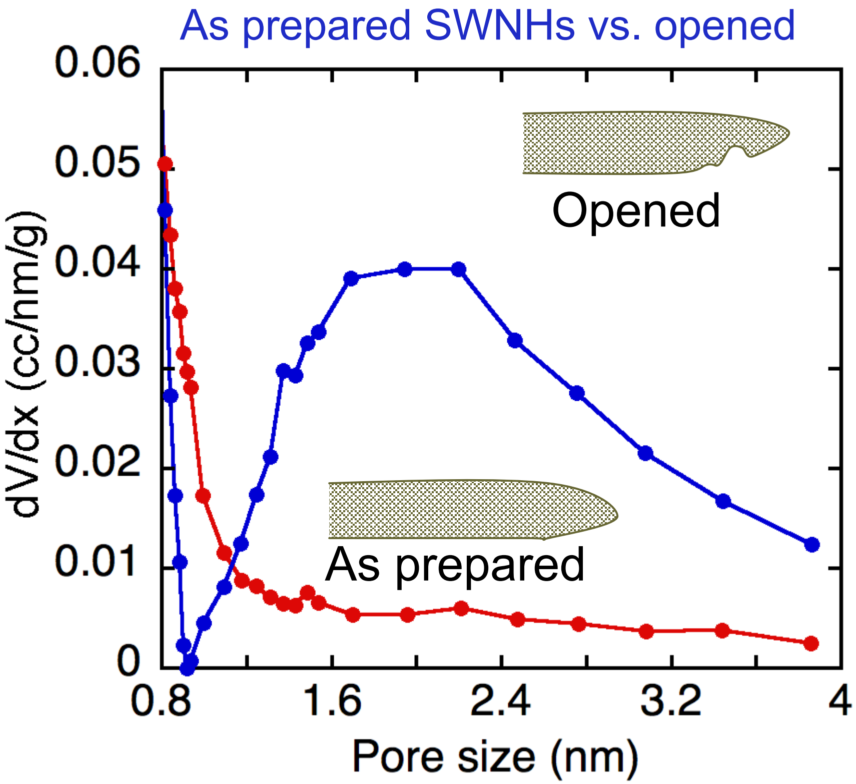
After pressing and annealing (2100C)

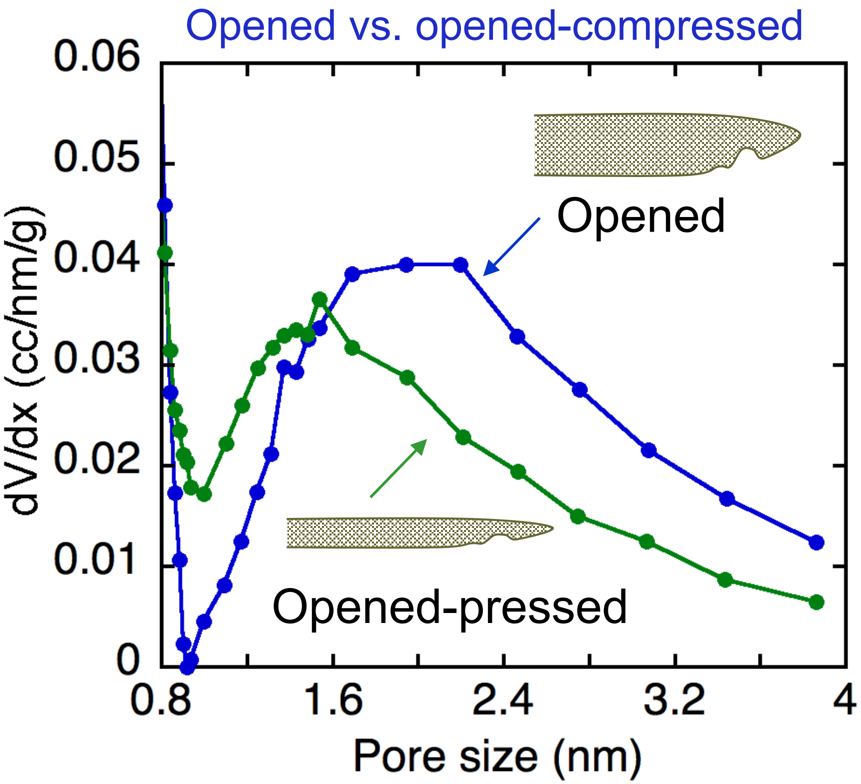




SWNHs pellet

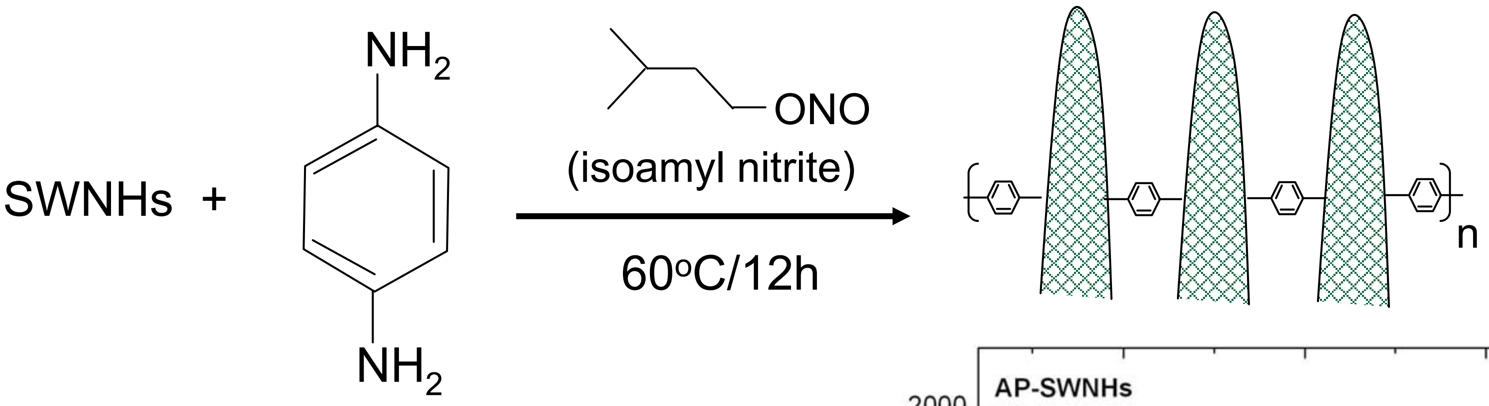
Controlling Porosity of Carbon Nanohorns: Measurements of Pore Size Distributions

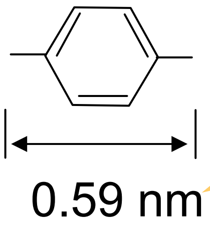




Tuning of pore sizes and surface areas of SWNHs has been demonstrated through oxidation, compression, and thermal treatments. A dedicated Quantachrome unit has been installed at ORNL this year to optimize surface areas and adjust pore sizes.

3-D Nano-Engineering for Pore-size Adjustment – Chemical Functionalization of SWNHs

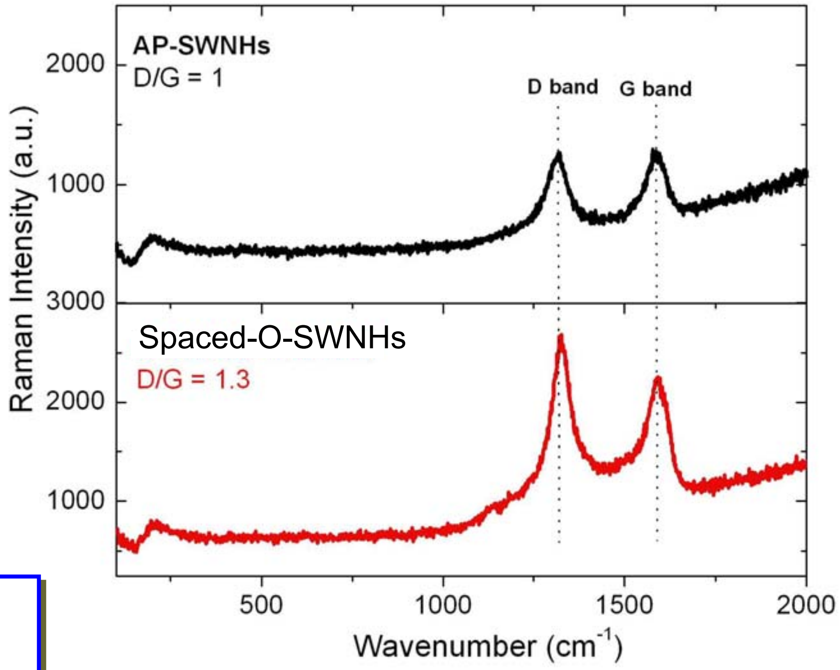




suitable interstitial size for hydrogen storage

C-C sigma bond length = 0.154 nm
C=C (benzene ring) bond length = 0.139 nm

Chemical spacers were introduced to adjust and control the pore sizes of SWNHs



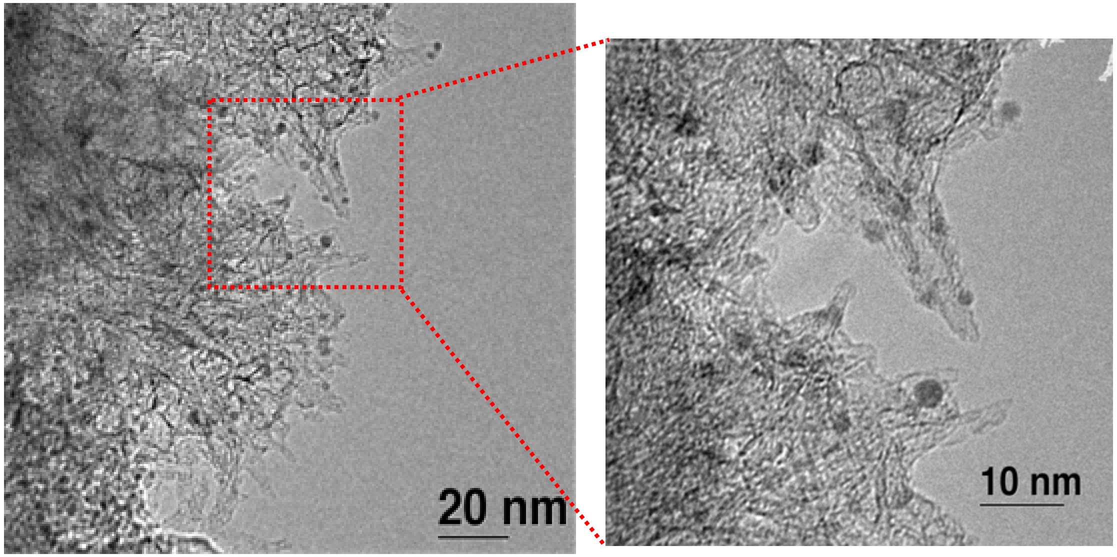
Increased D/G ratio in the Raman spectra indicates the increased number of defects due to chemical functionalization.

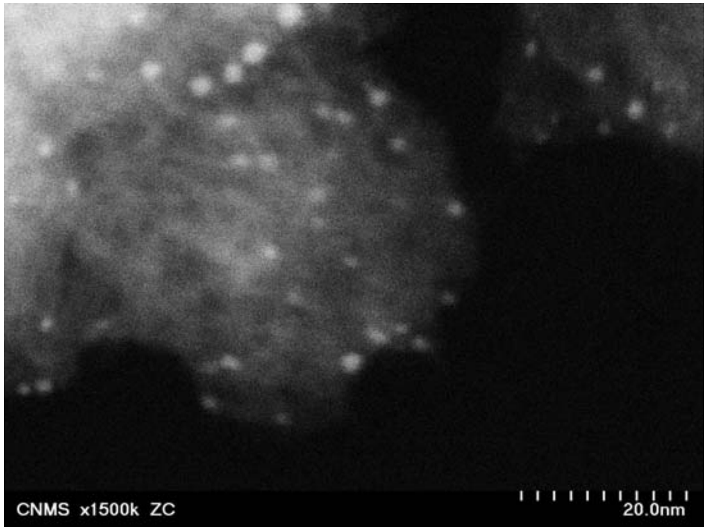
Pd Decoration of opened SWNHs (O-SWNHs) by Wet Chemistry Method

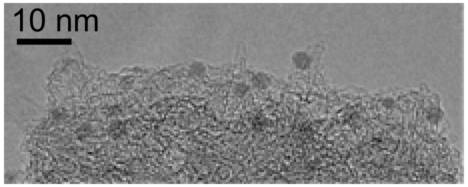
$$H_2PdCl_4 + \text{EtOH/PVP} \xrightarrow{80^{o}C} \text{Pd NP} \xrightarrow{\text{O-SWNHs}} \text{O-SWNHs/Pd-CH}$$

Ref: *Bekyarova, et. al. JPCB, 2005*

(Pd decorated opened SWNHs via chemistry)





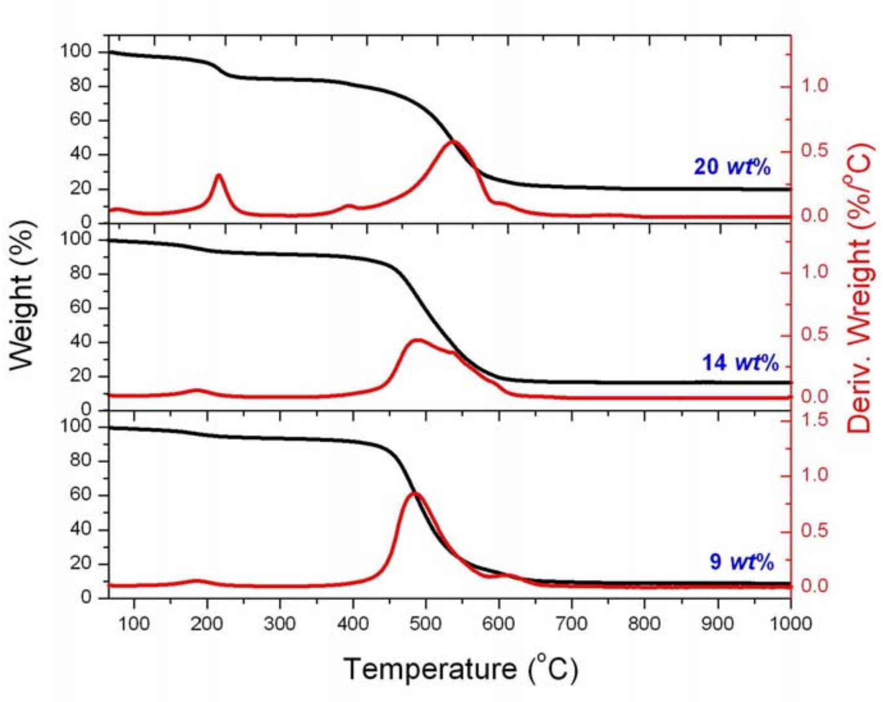


- *Pd size: 1-5 nm.*
- *Pd loading in O-SWNHs/Pd-CH is 2.6wt% (PGAA by NIST)*

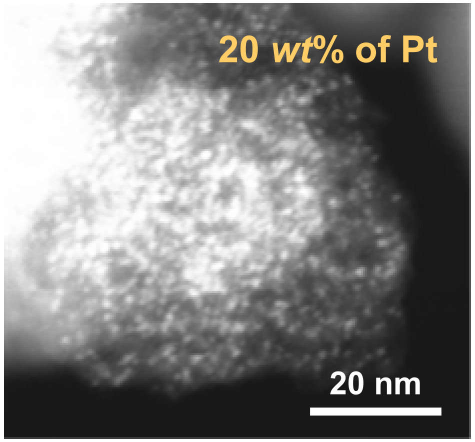
Wet chemical treatments to uniformly decorate O-SWNHs with Pd nanoparticles were developed.

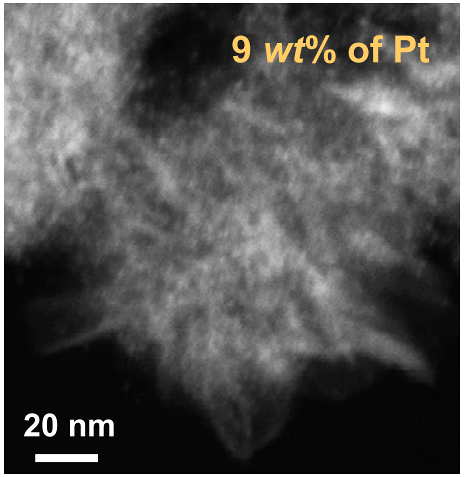
Controlled Decoration of Opened SWNHs (O-SWNHs) with Different Loading of Pt Nanoparticles

$$H_2PtCl_6 + \text{O-SWNHs} \xrightarrow[80^{o}C]{\text{sodium citrate}} \text{O-SWNHs/Pt-CH}$$



Z contrast STEM images of O-SWNHs/Pt-CH with controlled Pt decoration:



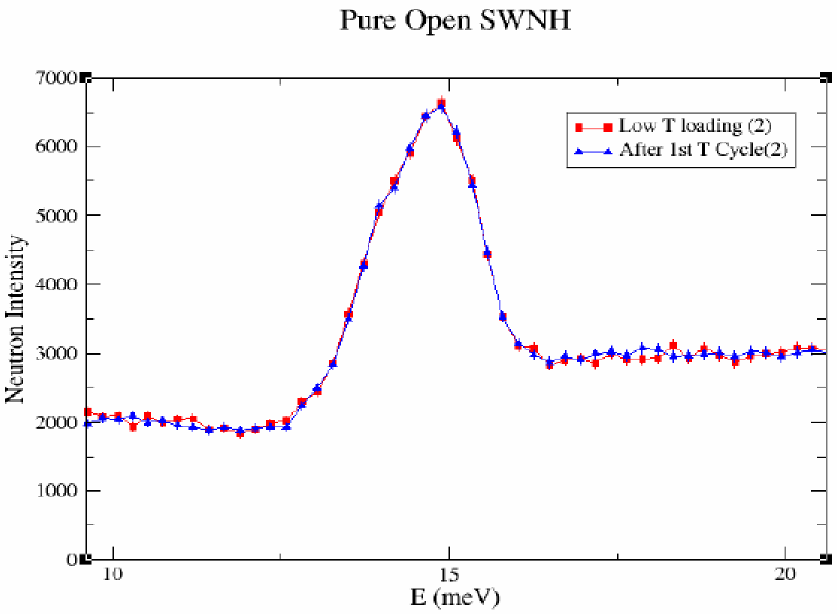


Tuning the surface area and pore size of SWNHs permits the loading of Pt on O-SWNHs to be varied from 9 wt% to 20 wt% *via* controlled chemical processing.

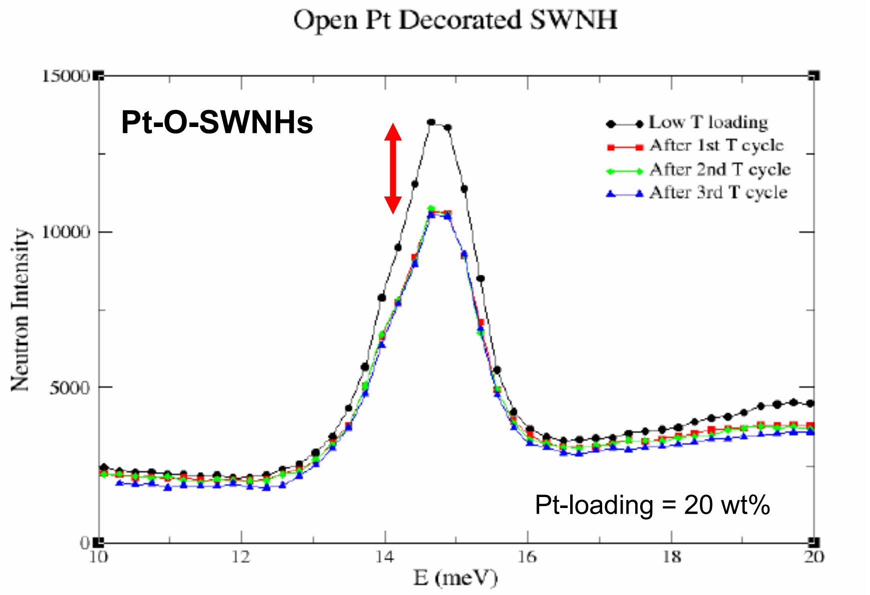
"Spillover" of Metal (Pt, Pd) Decorated Opened SWNHs – *Neutron Scattering Measurements by NIST*

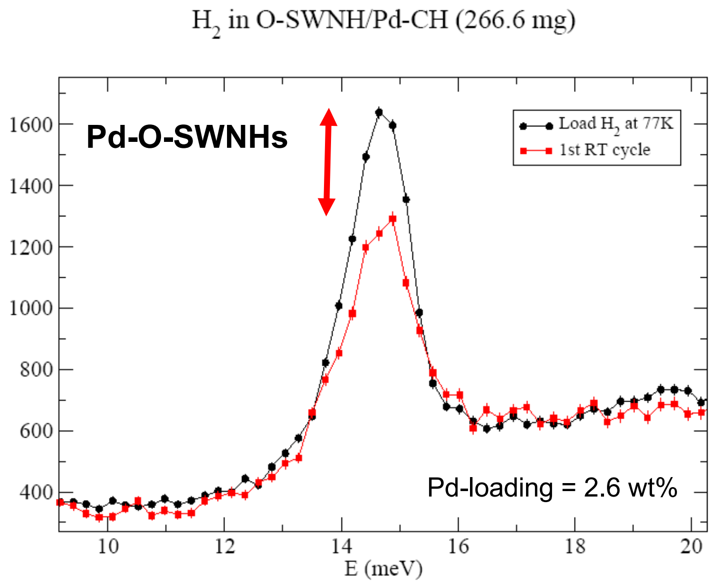
Method:

(1) Load H_2 at 77K and cool to 4K. Measure the rotational transition peak (RTP).
(2) Heat the sample up to room temperature and wait for 1 day and cool down to 4 K. (This is one temperature cycle).
(3) Compare RTP before and after one cycle.


Pure Open SWNH

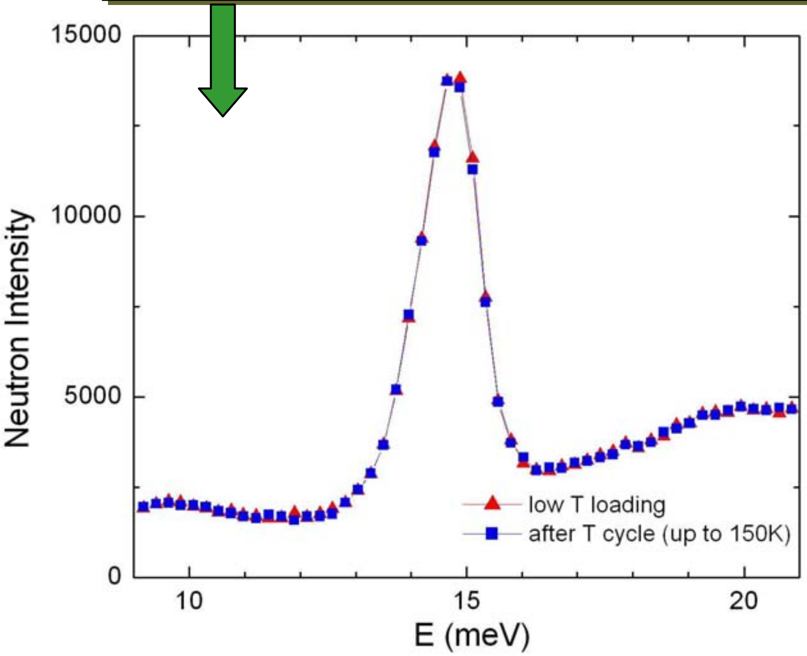
Metal catalyst (Pt- and Pd-) decorated nanohorns show clear evidence for room temperature conversion of H_2 to other forms, and storage (while no change has been observed in pure SWNHs).


Open Pt Decorated SWNH

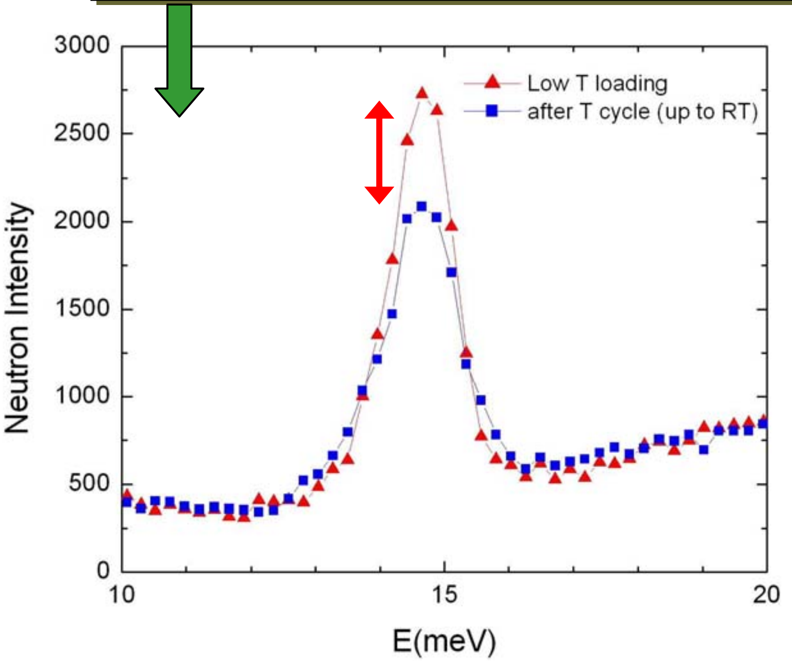

H_2 in O-SWNH/Pd-CH (266.6 mg)

“Spillover” of Pt Decorated Opened SWNHs (O-SWNHs/Pt-CH) – *Neutron Scattering Measurements by NIST*

Method:
(1) Load H_2 at 77K, cool to 4K. Measure the rotational transition peak (RTP).
(2) Heat the sample up to 150K and wait for 40 mins. Cool to 4K.
(3) Measure RTP again and compare.

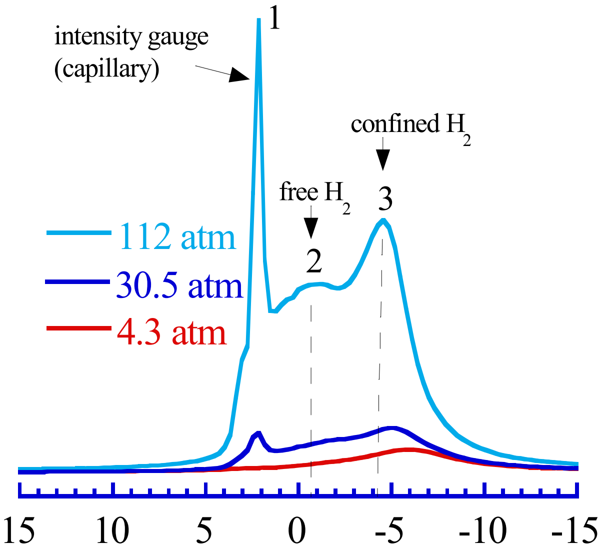


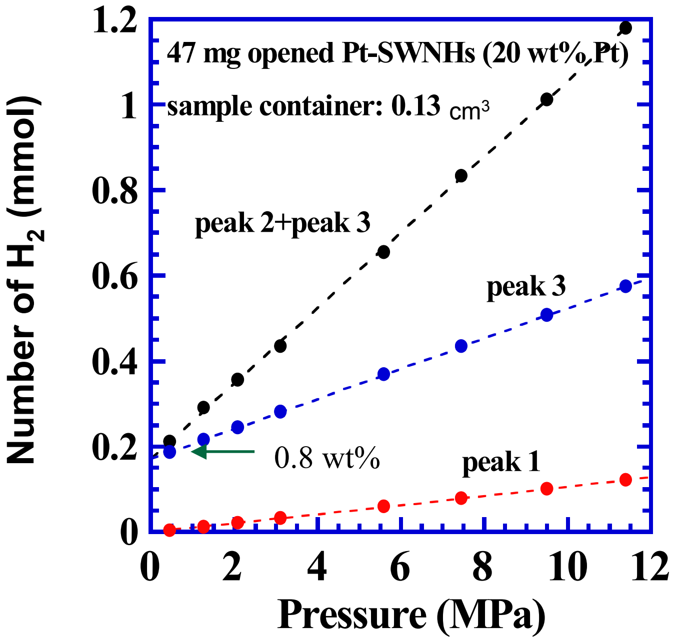
Method:
(1) Load H_2 at 77K, cool to 4K. Measure the rotational transition peak (RTP).
(2) Heat the sample up to 298K and wait for 1 day and cool to 4K. (one cycle)
(3) Measure RTP again and compare.

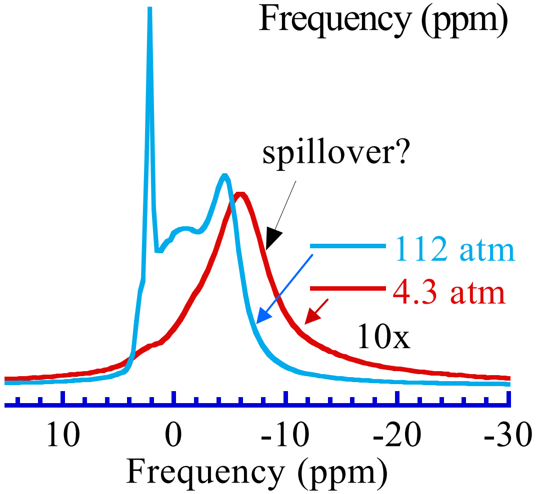


“Spillover” measurements repeated on the 1-gram sample scale confirm that Pt-decorated SWNHs dissociate H_2 at with an onset temperature somewhere between 150K < T < 298K.

NMR Measurements of Adsorbed Hydrogen in Pt-Decorated SWNHs – *by UNC*

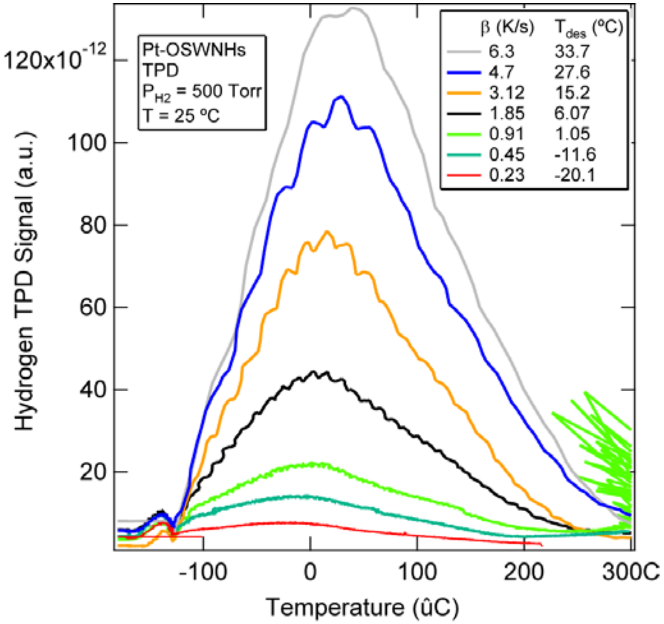




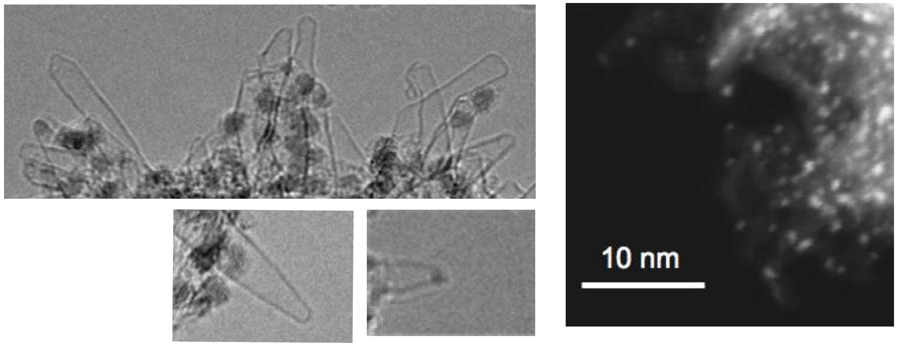


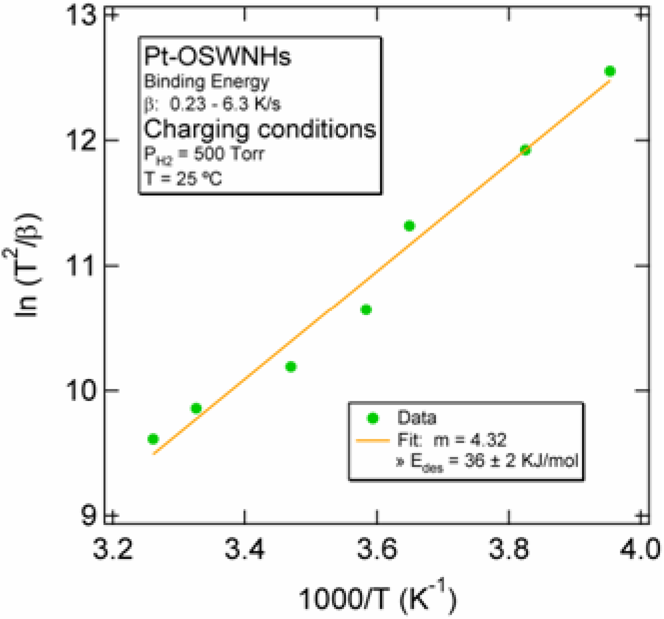
- NMR measurements can distinguish free hydrogen from confined/adsorbed hydrogen.
- Room temperature adsorption/confinement increases from 0.8 wt% at 4.3 atm to 2.6 wt% at 112 atm.

Increased Binding Energy for H_2 - 36 kJ/mol:
H_2 TPD Measurement of Pt-Decorated Opened SWNHs – *by NREL*



H_2 TPD as a function of heating rate (β) for O-SWNHs/Pt-CH.



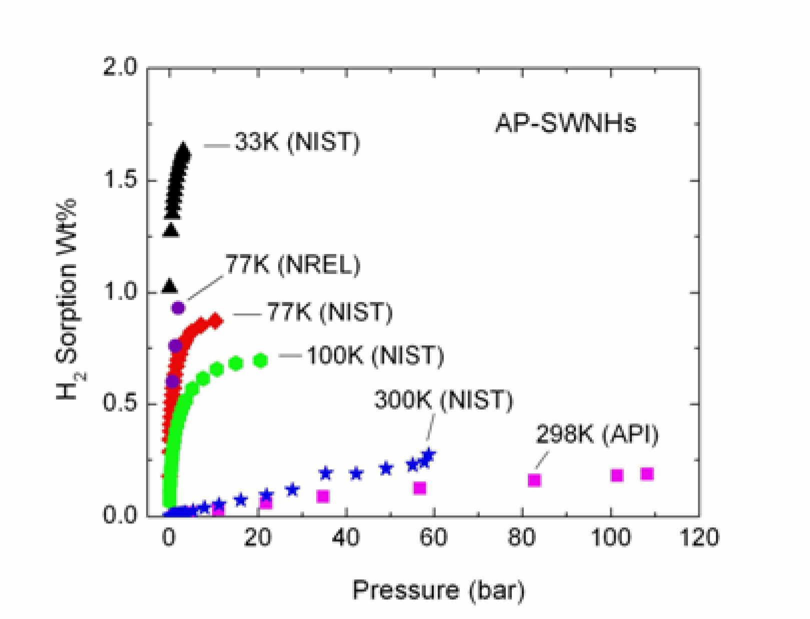


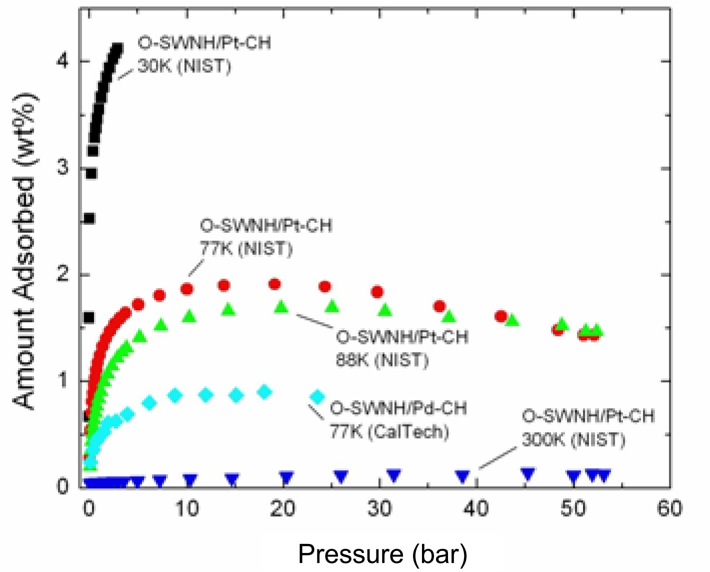
Temperature programmed desorption of Pt-decorated nanohorns (O-SWNHs/Pt-CH) shows a ~ room temperature H_2 peak and a binding energy of 36 kJ/mol.

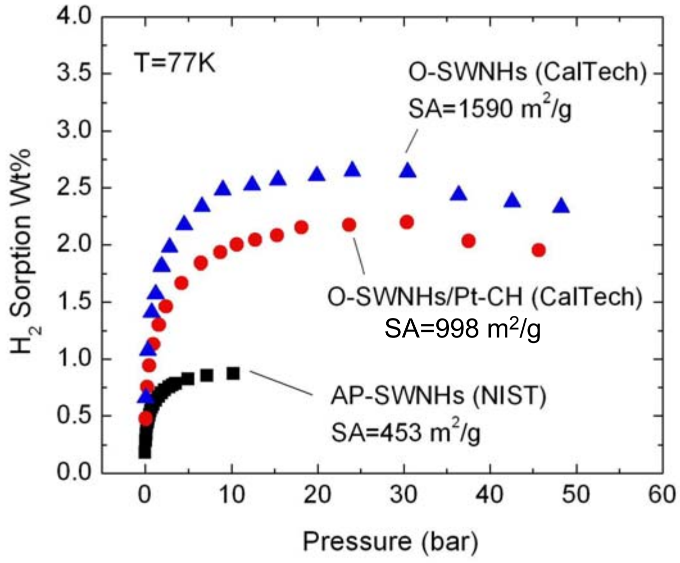
Kissinger plot showed the desorption barrier energy E_{des} = 36±2 kJ/mol

Jeff Blackburn, et al.,- NREL

Hydrogen Isotherm Comparisons on As prepared SWNHs (AP-SWNHs), Pt decorated SWNHs (SWNHs/Pt) and Opened SWNHs (O-SWNHs)



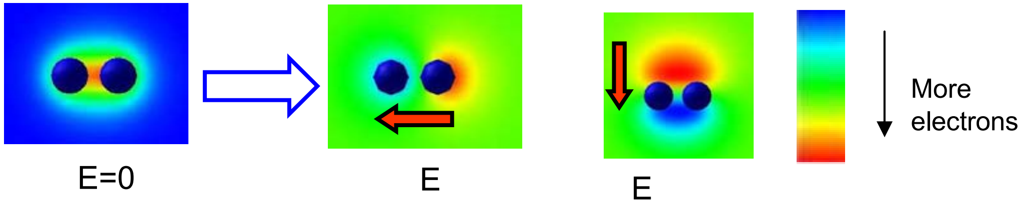




- **O-SWNHs have 3X uptake of unopened AP-SWNHs.**
- **O-SWNHs/Pt-CH has lower hydrogen uptake (2 wt%) compared to O-SWNHs (2.6wt%) due to the possible decrease of surface area by Pt particles.**

New Direction - Charging Nanostructures for Increased Hydrogen Storage

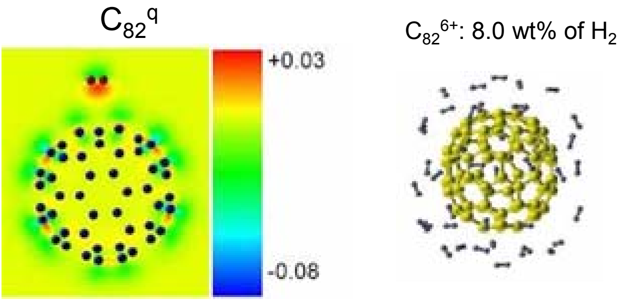
- **Our theory predicts distributed charges over nanostructures lead to increased binding energies and significant hydrogen storage**



Origin: Polarization of hydrogen molecule under an external electric field

$\Delta \rho = [\rho(H_2 \text{ under } E=0) - \rho(H_2 \text{ under } E \neq 0)]$

- **Example: Charging a fullerene :**
  $6e^-$ on C_{82} can store 8 wt.% H_2



- Mean hydrogen binding energy of 0.18 to 0.19 eV/H_2
- Smaller fullerenes require less charges

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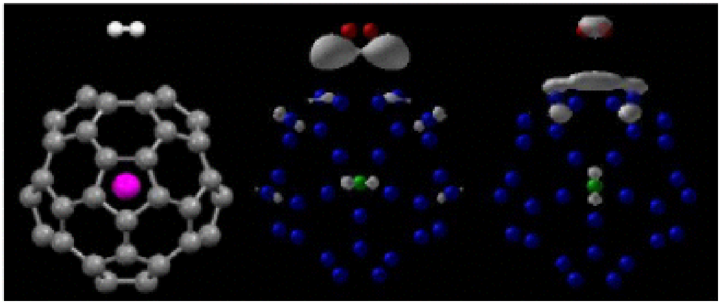
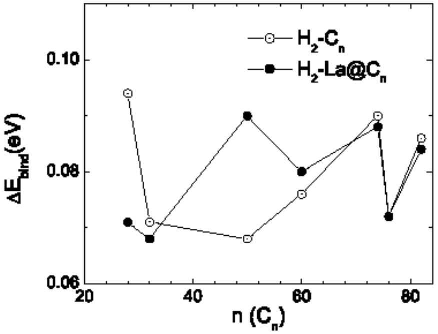
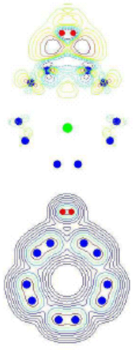
Example: Single metal atoms inside nanostructures can charge their outer surfaces, greatly affecting the binding of H_2

- Metal decoration leads to charging of entire surface, polarizing H_2
- Significant binding energy increase for some n
- Can nanostructures be filled or decorated to optimize this effect?
- We will explore this effect.

[Example: Metallofullerene (e.g. La@C_{50})]







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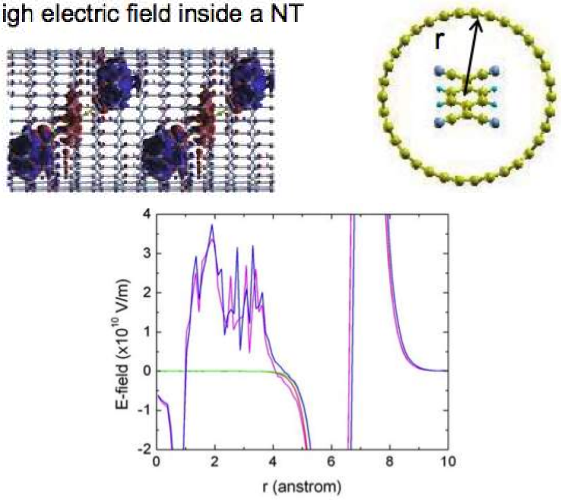
New Direction - Charging Nanostructures for Increased Hydrogen Storage

- **Chemical processing and decoration of nanostructures can lead to significant charging of nanostructures (inadvertent or intentional). Our theory indicates this effect can be tuned to enhance hydrogen storage**
  - **Metals**
    - Endohedral or exohedral decoration of metal atoms lead to charged nanostructures (explanation of spillover mechanism?)
  - **Adsorbates**
    - Molecules (inside and outside nanostructures) may be as effective as substitutional dopants
  - **Electrochemical oxidation/reduction?**
    - Chemical functionalization (e.g. redox state of PANI, acid groups on NT)
  - ***Can we form a supercapacitor storage medium?***

Organic molecules inside nanostructures can generate sufficient E-fields for H_2 storage. (e.g. TCNQ @ (17,0) SWNT)

High electric field inside a NT



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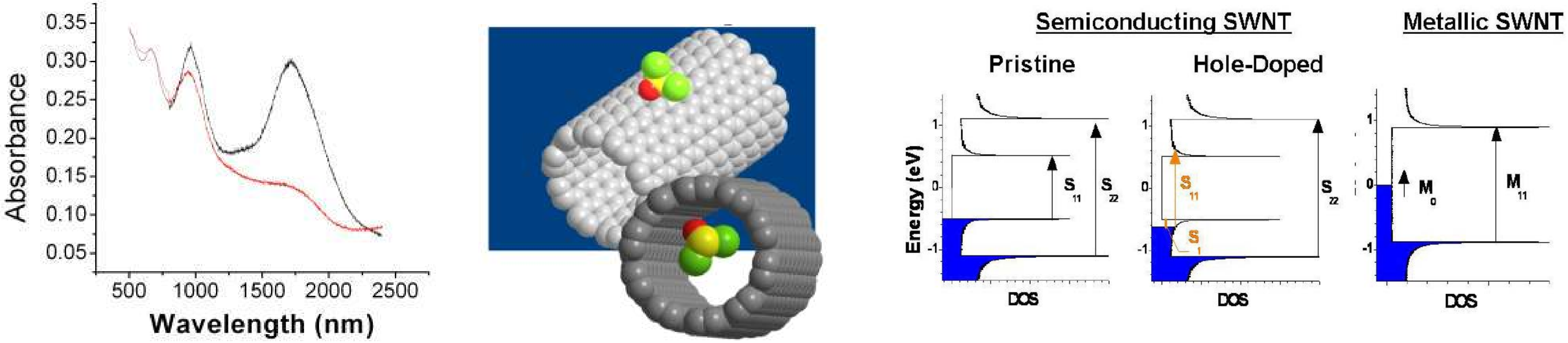

Charging of SWNTs due to doping by small molecule adsorbates

Future Work

- **Next steps during FY 2007:**
  - **Understand benefits of metal decoration** *(spillover vs. charge transfer doping, direct storage on metals).*
    - Clarify mechanisms *(with NIST, NREL, and UNC)* responsible for enhanced storage, increased binding energy, and linear storage density behavior in metal decorated samples. *Milestone 9/07 (work in progress)* *Identify dominant mechanisms responsible for hydrogen storage in metal-decorated samples*
  - **Tuning porosity and surface area**
    - Implement further mechanical, thermal, and chemical treatments to adjust sub-nm pores for increased storage. Implement CO_2 and Ar BET tests at ORNL to correlate optimal pore sizes correlating with increased hydrogen uptake, and screen effects of processing on pore blockage prior to partner testing of samples. *Milestone 9/07 (work in progress)* *Adjustment of processing conditions for optimal gravimetric storage.*
    - Continue to assess the effects of compression (to address volumetric storage targets) on pore size, blockage, and surface area.
    - Interact with partners for theoretical predictions of optimal pore sizes *(Rice U., NREL)*
  - **Charged nanostructures for enhanced hydrogen storage**
    - Explore charged nanostructures and composites for comparison with our theoretical predictions for enhanced storage. *(New direction)* First: Well-specified charge transfer doping experiments.

Future Work

- **FY 2008:**
  - **Decision Points**
    - 9/07 - Assessment of spillover: Clarify mechanism and preliminary data (ours and Center-wide). Understand the interplay between support, organic “bridges”, and metal nanoparticles in order to design optimal nanocomposite for hydrogen storage.
  - **Engineer nanocomposites tailored to achieve DOE targets for hydrogen adsorption**
    - **Charged Nanostructures** - In accordance with our theory and modeling, utilize organic materials with large dipole moments to dope nanohorns and other high surface area supports to create high local electric fields and utilize charged surfaces to polarize and store H_2
    - **Spillover** - Determine form of stored hydrogen (atomic vs. molecular) in spillover measurements, and method of release. If protonation occurs, design supercapacitor-like nanocomposites to enhance this effect.
    - **Supercritical Adsorption -** Explore (with theory and experiment) the use of metal atoms and charge to stabilize molecular clusters of hydrogen at supercritical temperatures. Utilize optimal pore sizes to stabilize hydrogen at liquid or higher density.

Summary Table

	Production Rate (g/hr)	SWNHs Types Produced		Surface Area (m^2/g)	Pore Size (nm)	Hydrogen Uptake (wt%)		Volumetric Density (g/L)
						300K	77K	
FY’05	<1	as prepared by laser	AP-SWNHs	-	-	-		-
FY’06	9	as prepared by laser	AP-SWNHs	453	-	0.2	1.0	
		Pt decorated by laser	SWNHs / Pt-LA			0.22	1.0	
		Pt decorated by chemistry	SWNHs / Pt-CH			0.28		
		opened by oxidation	O-SWNHs	1590	1.5-1.7		2.6	
		opened and Pt decorated	O-SWNHs / Pt-CH				2.2	13

Summary Table (Cont.)

	Production Rate (g/hr)	SWNHs Types Produced		Surface Area (m^2/g)	Pore Size (nm)	Hydrogen Uptake (wt%)		Binding Energy (kJ/mol)	Volumetric Density (g/L)
						300K	77K		
FY'07	20	Pressed opened (air)	P-O-SWNHs	1244	0.35, 0.55, 0.82, 1.4, 1.8, 3	*	*	*	31
		CO_2 opened	O-SWNHs (CO_2)	1860	*	*	*	*	*
		opened and Pt decorated by chemistry (20wt% Pt)	O-SWNHs / Pt-CH (20 wt%)	998	*	0.3 - 0.8	2 - 3.5	7.1 36 ± 2	*
		opened and Pd decorated by chemistry (3 wt%Pd)	O-SWNHs/ Pd-CH	637	*	*	1.0	*	*
System Target							6 in 2010		45 in 2010

* Measurements in progress

Metal-decorated SWNHs are yielding increased adsorption and binding energies compared to undecorated materials with equivalent surface area. Processing techniques to preserve high surface areas during metal decoration and pore size adjustment are underway.

Summary

- **Single-walled carbon nanohorns (SWNHs) are an economical medium with tunable porosity to support metal catalyst nanoparticles to explore metal-assisted hydrogen storage.**
  - SWNHs are produced metal-free, in high yields, with variable, controllable morphology at 20g/hr rates using a 600W laser with tunable pulse width.
  - Chemistry has been developed to decorate SWNHs with 1-5 nm nanoparticles to 20% (Pt) and 2.6% (Pd) weight loadings (in gram quantities) to probe spillover and metal-assisted hydrogen storage mechanisms.
  - Surface areas, pore sizes, and pore volumes are being adjusted through new oxidation (CO_2) procedures - surface areas up to 1900 m^2/g have been achieved.
  - Metal decoration (both Pt and Pd) in SWNHs yields a “spillover” effect, as discovered by neutron scattering at NIST. This was reproduced on 1g samples.
  - Binding energies of 7.1 and 36±2 kJ/mol for Pt-decorated SWNHs measured (NMR & TPD).
  - Hydrogen storage densities at present vary 0.2–0.8 wt.% at 298K, 1–3.5 wt.% at 77K.
  - Pressed SWNHs pellets with densities > 1 g/cm^3 demonstrated, estimated volumetric storage densities of 31 g/L.
  - The effects of electric fields on hydrogen storage have been investigated through theory and simulation. High field strengths sufficient to polarize and bind H_2 were found to occur through the addition of charge to nanostructures resulting from metal atom decoration or organic molecule intercalation. New directions for controllable doping and charging of nanostructures to enhance this effect were derived from these studies.