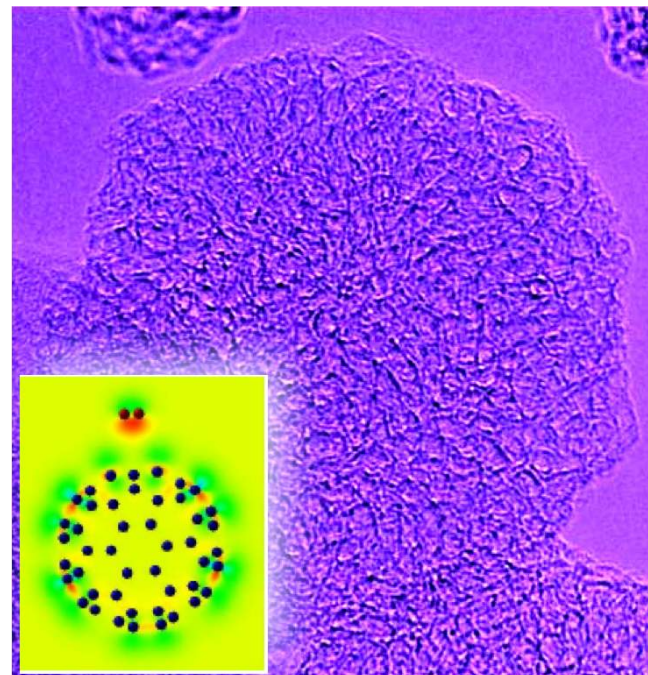


Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

David B. Geohegan, PI
Alex Puretzky, Mina Yoon, Chris Rouleau
Hui Hu, Bin Zhao and Karren More

*Materials Science and Technology Division,
Center for Nanophase Materials Sciences,
and the SHaRE User Facility*

Oak Ridge National Laboratory, Oak Ridge, TN



Project ID ST-20

DOE Hydrogen Program Annual Merit Review, June 11, 2008

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- 70% complete

Budget

- Total project funding
 - DOE share 1.6 M\$
 - Contractor share 0k
- 300k received in FY07
- 400k for FY08

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 sorption - Air Products, NREL, NIST, CalTech
 - Neutron scattering - NIST
 - NMR - UNC
 - Nanoarchitectures - Rice

Objectives

Overall

To exploit the tunable porosity and excellent metal supportability of *single-walled carbon nanohorns* to optimize hydrogen uptake and binding energy.

2007

Controllable tuning of SWNH size and porosity by adjustment of synthesis conditions. Development of methods to activate and metal-decorate SWNHs. Understand the dominant mechanisms of H-storage required to meet DOE targets.

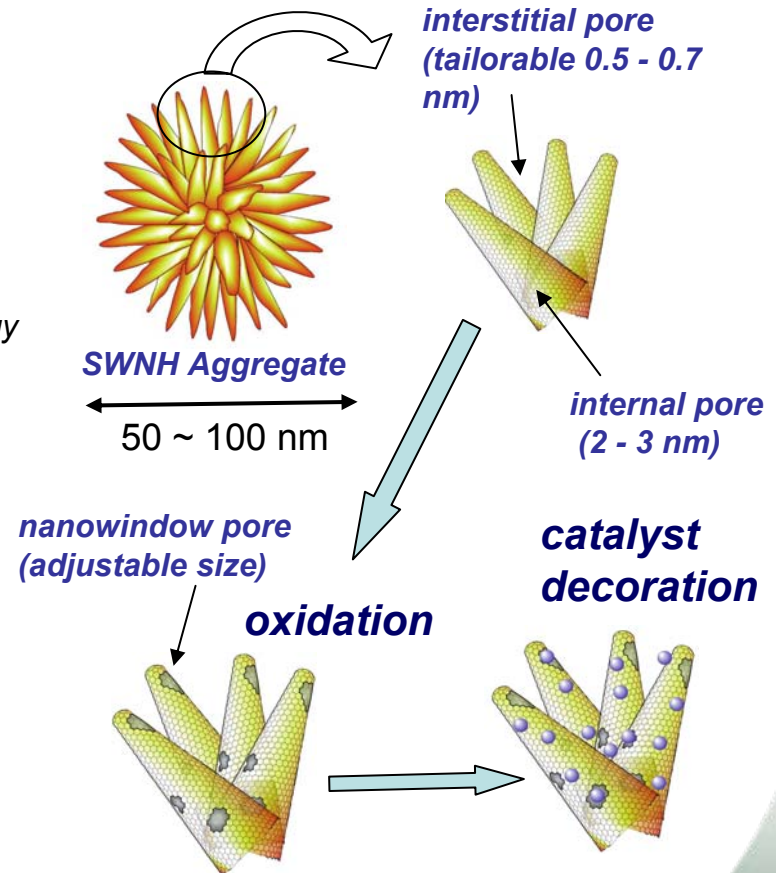
- ✓ Developed efficient, scalable production - tunable morphologies.
- ✓ Metal decoration - Pt, Pd results in spillover, enhanced binding energy
- ✓ Encouraging uptake - 3.0 wt.% @77K, 0.3 - 1.5 wt.% @RT,
- ✓ Compression - 1.03 g/cm³, 30 g/L volumetric

SWNH pellet
1.03 g/cm³



2008

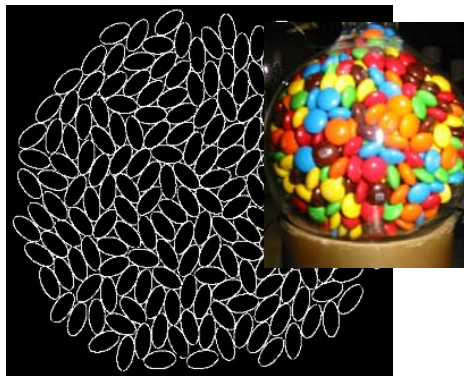
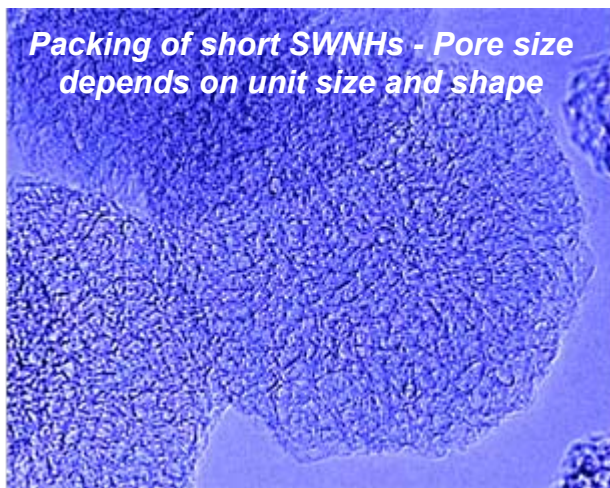
- Improve surface area to 2200 m²/g for > 3.0 wt.% at 77K
- Adjust pore sizes controllably to < 1 nm
- Quantify effects of pore size on storage
- Theoretically investigate origin of binding energy increase
- Search for alternate metals to enhance binding energy
- Develop new synthesis/decoration approaches for these materials.



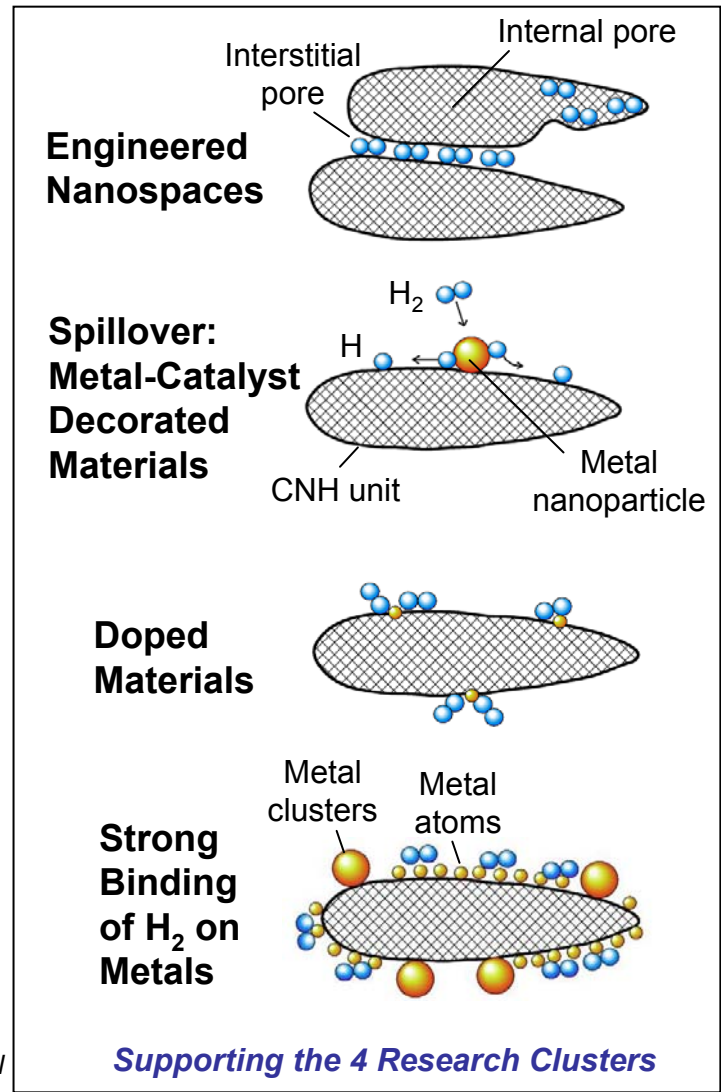
Approach

Bottom-up synthesis approach:

- Form well-defined nanostructures with tailored properties (e.g. preferred adsorption sites in tips of SWNHs, variable internal pores, ...)
- Assemble architectures with tailorable interstitial pores, and with metals to enhance binding energies.
- Utilize SWNHs: Maximal surface area, pure C but excellent metal support, self-assembles into highly-organized observable architectures.



Monte Carlo simulation of Packed m&m's
Chaikin group, NYU web page
www.physics.nyu.edu/~pc86/packing.html



SWNH structure is tailored, decorated with metals, and assembled into different architectures to explore enhanced H₂ storage: *New focus on charged nanostructures.*

Milestones and Tasks

Task 1: Controlled Synthesis of SWNHs with Tunable Pore Sizes by Laser Vaporization

- Single-wall carbon nanohorns (SWNHs) with tunable morphologies were synthesized and delivered to partners, along with metal-decorated samples.
- Adjusted pores from 1.7 nm to < 1 nm.

Milestone Achieved 3/08
Vary synthesis conditions to tailor pores and morphology to sub-nm with high surface areas, delivered to partners

Task 2: Controlled Processing of SWNHs for Tunable Porosity, Surface Area, and Graphitic Structure for H Storage and Catalyst Supports

- Improvements in activation yielded high surface areas (2142 m²/g) and 3.5 wt.% at 77K.
- Pore size analyses performed verifying tunable porosity following synthesis and processing.

Milestone Achieved 5/08
*Characterization of pore size, nanostructure, graphitic content, and effects on surface area and uptake.
Improve surface area to 2200 m²/g to obtain uptake > 3.0 wt.% at 77K.*

Task 3: Theoretical Search for the Optimal Hydrogen Storage Material

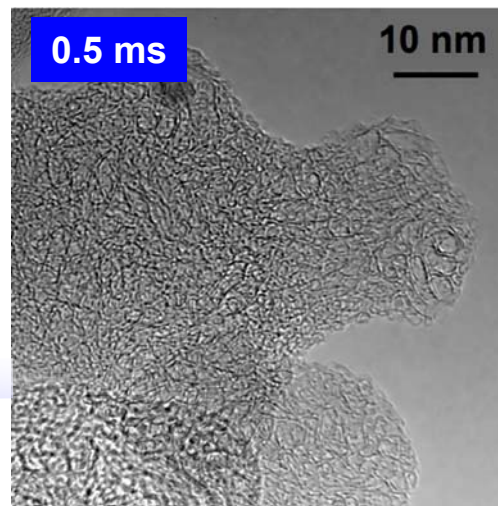
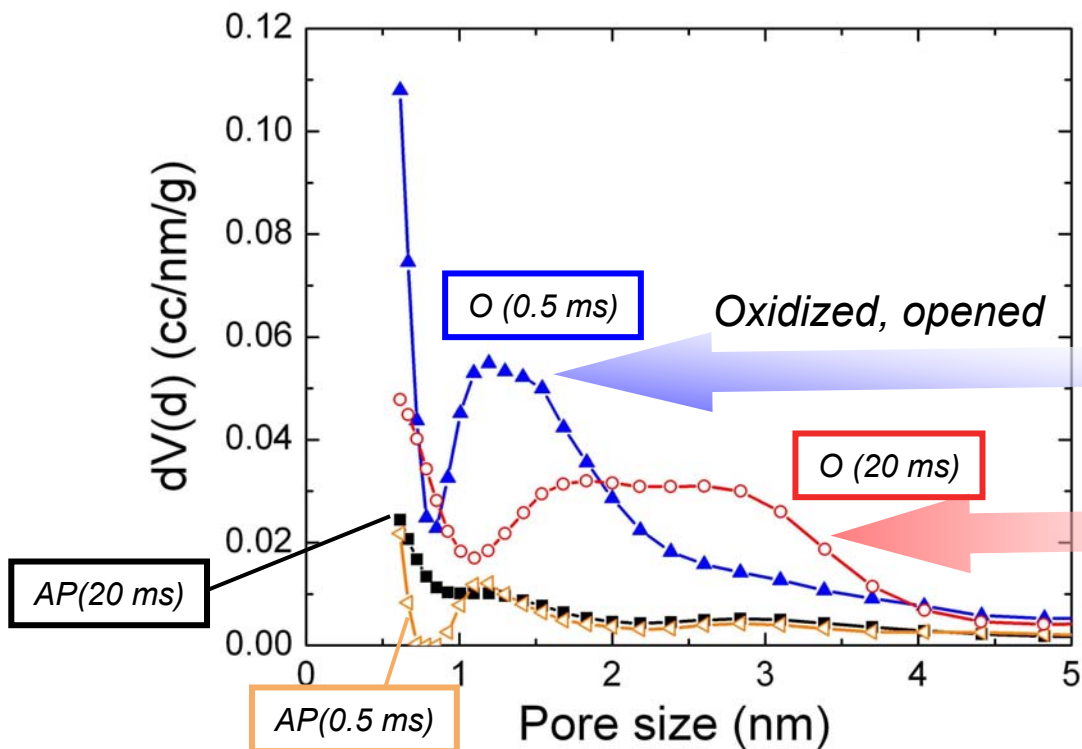
- Theoretical search performed for alternatives to transition metals for increased binding energy and minimized clustering.
- Cluster formation mechanisms identified for transition metals.
- Alkaline earth metals Ca and Sr identified to bind H₂ by polarization resulting from dipole fields.
- Ca-decorated C predicted optimal: 8.4 wt.% and 0.4 eV
- Synthesized Ca-decorated SWNHs
- New storage mechanism opens options for design of many new nanostructured materials. Several identified: (e.g. TCNQ-SWNTs, TTF-TCNQ, ...)

Milestone Achieved 3/08
Theoretical search for new metal alternatives with promise for H₂ storage and binding energy enhancements based upon charged nanostructures. Quantitative uptake and binding energy estimates performed.

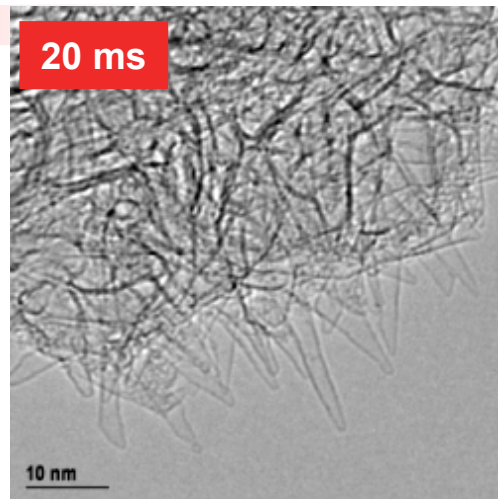
Milestones in Progress 6/08 and 9/08
Clustering mechanisms for TMs calculated. Designs for nanostructures with large dipole moments for hydrogen polarization by strong electric fields

Milestone Progress for 9/08
Synthesize and test metal-alternative -decorated SWNHs

Adjusting Pore Sizes During Synthesis via Laser Pulse Width and Annealing at High Temperature



“short”



“long”

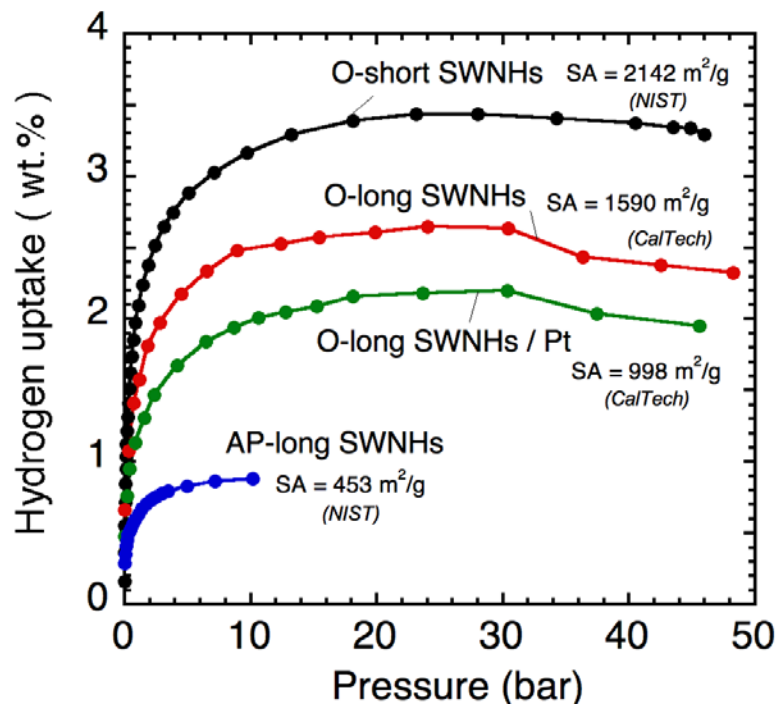


SWNHs synthesized for different periods at high temperatures have quite different pore size distributions. The interstitial pores and internal pores can be tuned by varying the ablation pulse width (plume temperature) and cooling time. The short SWNHs have narrower distributions, smaller pores.

Increased Surface Areas for Short O-SWNHs - Higher H₂ Adsorption Achieved

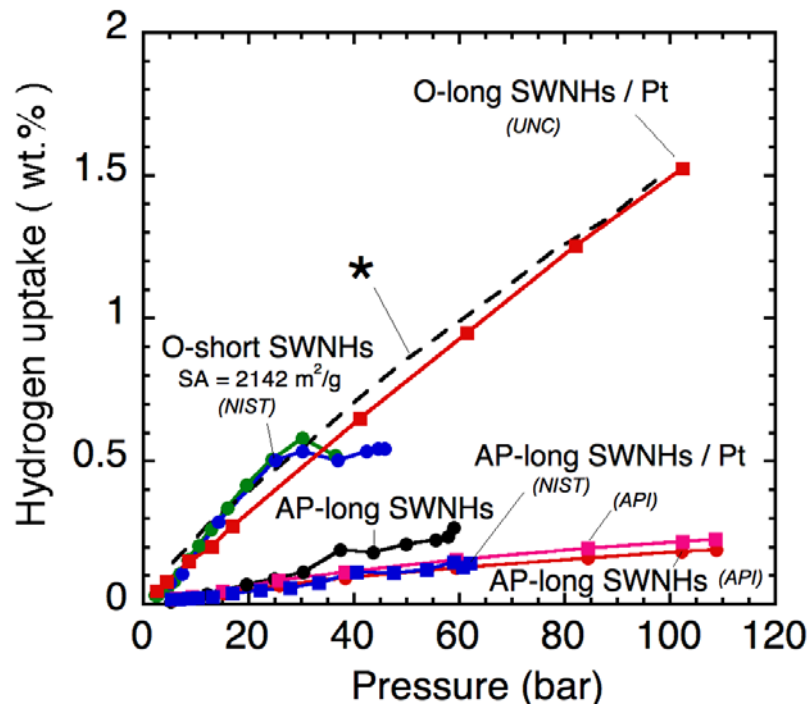


77K



Short O-SWNHs adsorb 3.5 wt.%
at 77K and 30 bar, better than
long O-SWNHs

Room Temperature

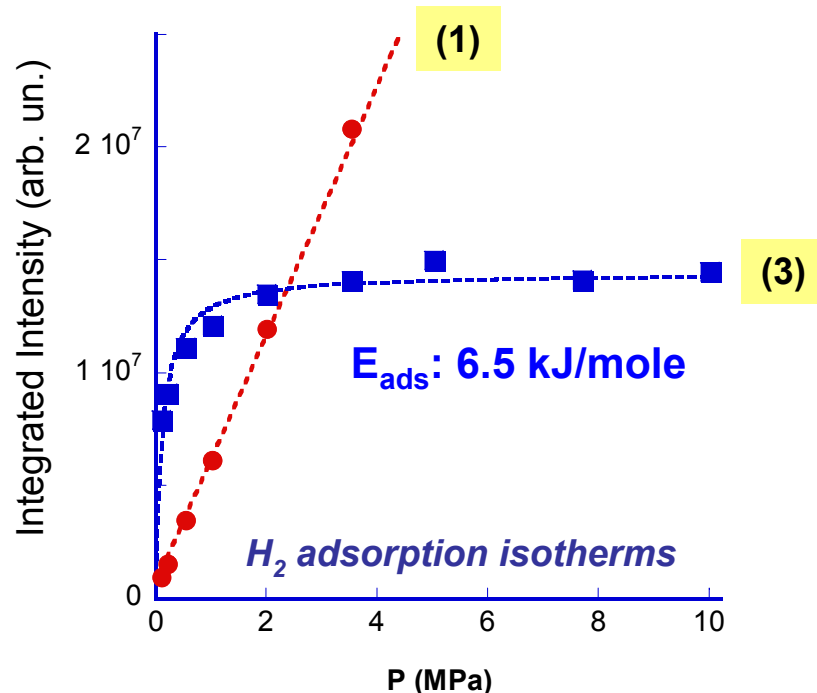
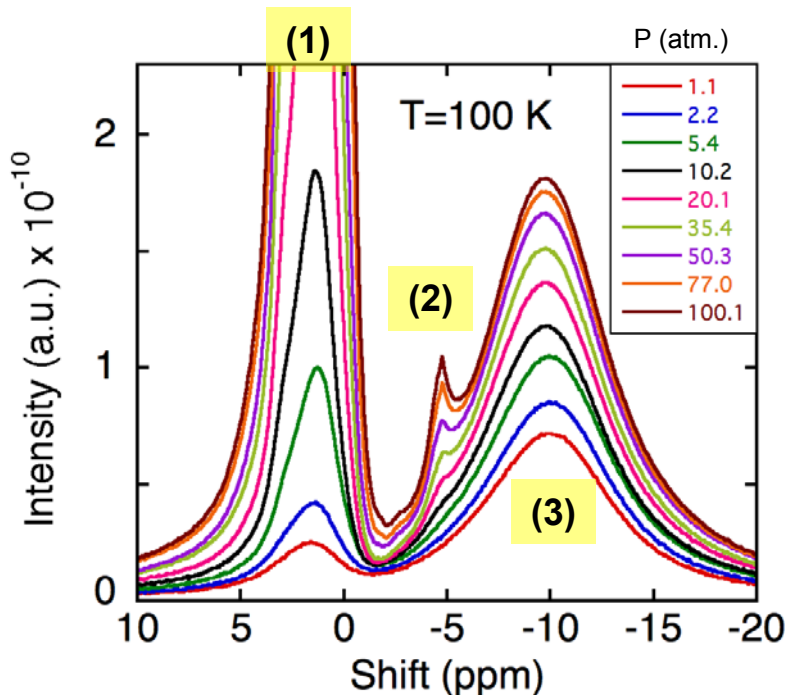


Short O-SWNHs adsorb 0.6 wt.%
at RT and 30 bar, comparable to
bridged MOFs

*Dashed line shows bridged MOF-177 (3100 m²/g)
Y. Li and R. T. Yang, *Langmuir* **23**, 12937 (2007).



NMR Measurements of Adsorbed Hydrogen in Short O-SWNHs

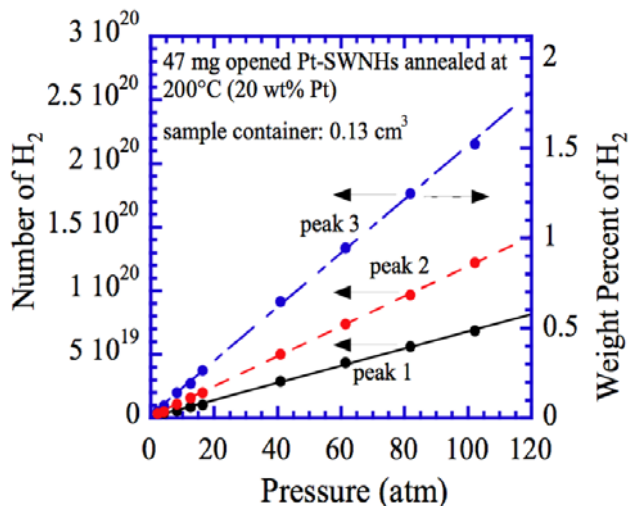


- Peak (1) - Free H₂ in NMR tube.
- Peak (3) - shows confined H₂ in narrow (~ 1 nm) micropores. This peak appears only in *opened* SWNHs, and has the largest peak shift of any sample studied by UNC.
- Room temperature spectra show the same lineshape, indicating that hydrogen is already confined.
- Peak (2) - possibly larger SWNH endohedral spaces ? Unclear.
- Isotherms for line (1) and (3) show Langmuir behavior with an adsorption energy of ~ 6.5 kJ/mole.

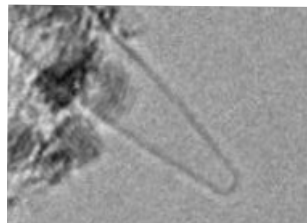
Short opened SWNHs store hydrogen nearly entirely within pores which are optimally sized (< 1 nm). O-SWNHs appear quite promising as a carbon scaffold for further doping or decoration with metals to increase the H₂ binding energy.

Metal (Pt)-Decorated “Long” O-SWNHs - Show Spillover and Enhanced Binding Energies

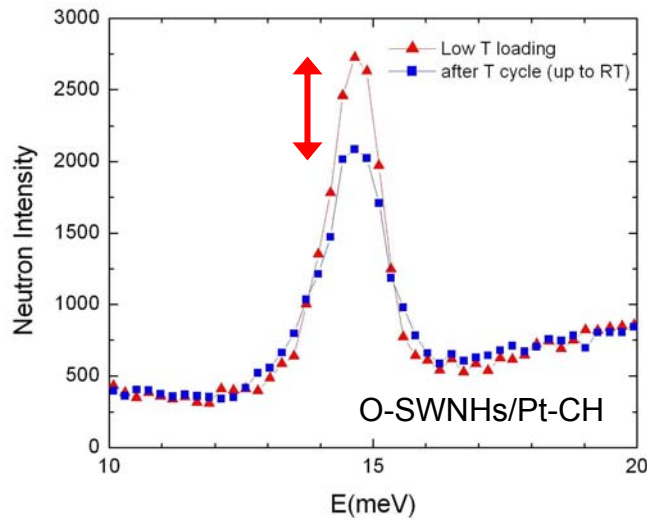
NMR measurements by UNC



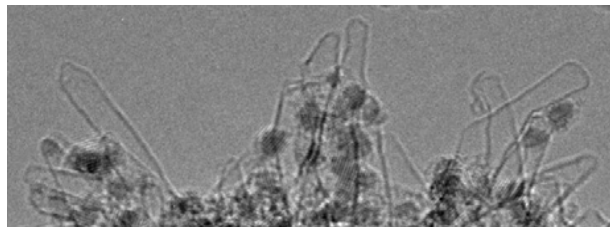
Room temperature adsorption / confinement increases linearly to 1.5 wt% at 100 atm.



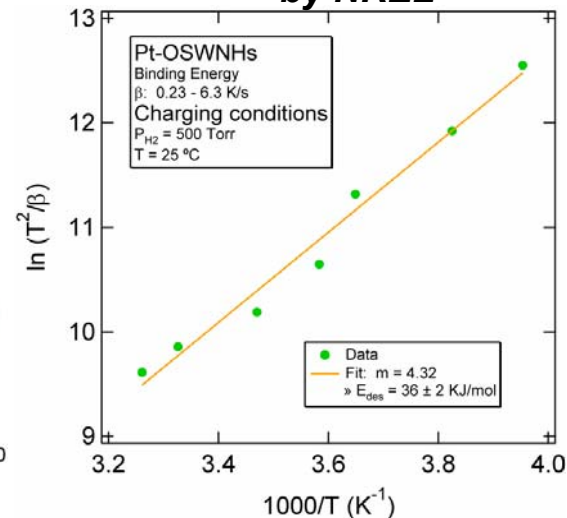
Neutron scattering measurements by NIST



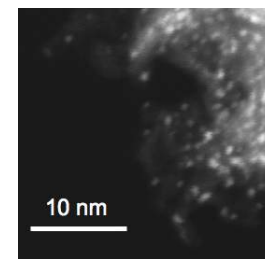
“Spillover” measurements confirm that Pt-decorated SWNHs dissociate H₂ with an onset temperature between 150K < T < 298K.



Temperature programmed desorption measurements by NREL



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

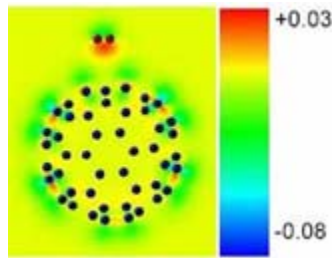


“Long” opened Pt-decorated SWNHs show promising results in RT hydrogen uptake, “spillover”, and increased H₂ binding energy

Origin of the Enhanced Binding Energy? Effect of Charging?

- Charged nanostructures can generate good and tunable H₂ binding sites:

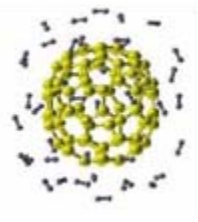
Example:



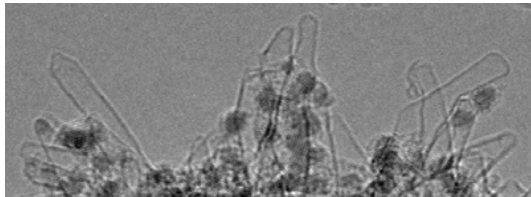
C₈₂⁶⁺: 8.0 wt% of H₂

H₂ binding energy: 10-30 kJ/mol

[M. Yoon, S. Yang, E. Wang, Z. Zhang, *Nano Lett.* 7, 2578 (2007)]



cf:

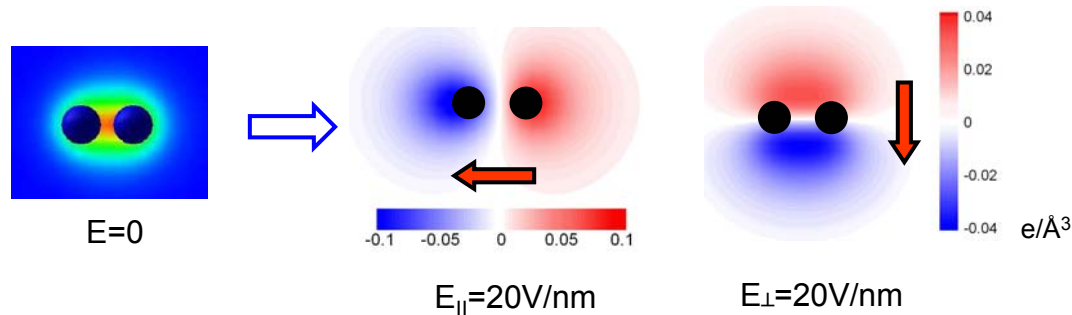


H₂ desorption energy barrier: 36±2kJ/mol

Metal decorated nanohorns: charged nanostructures?

- Origin of the strong hydrogen binding:

Polarization of H₂ under a high electric field produced by charged nanostructures

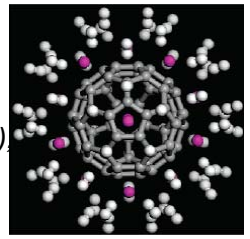


Can metal-decorated nanocarbons stabilize an electric field over their surfaces?

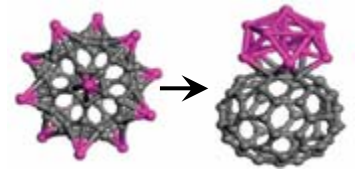
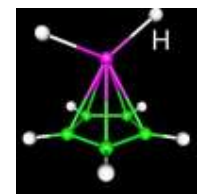
Searching for New Coating Metals to Distribute Charge

❖ Alkali metals: no clustering
too weak binding

[U. Zimmermann et al., Carbon 33, 995 (1995)
Q. Sun et al., JACS 128, 9741 (2006)]



❖ Transition metals: too reactive & clustering problem



[Y. Zhao et al. PRL 94, 155504 (2005)]

[JACS, 127, 14582(2005)]

How about Alkaline Earth metals ?

Criteria in searching alternative coating metals

- 1) Metal-Carbon interaction \geq Metal-Metal interaction:
prevention of metal clustering energetically and kinetically
- 2) Generation of active chemical sites:
right range of H_2 binding energy for ambient condition applications
- 3) Light elements: to meet the gravimetric capacity target

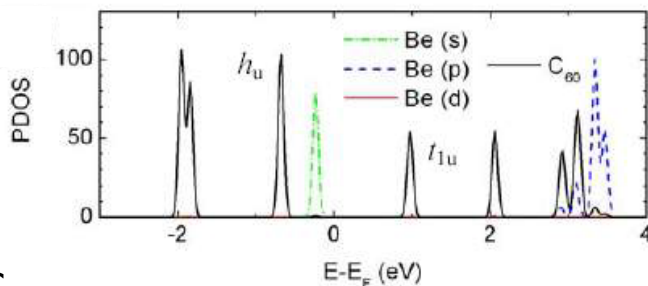
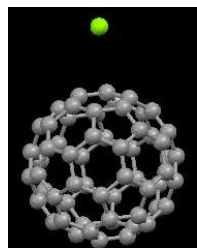
1 H hydrogen 1.008	2A																3A	4A
3 Li lithium 6.941	4 Be beryllium 9.012															5 B boron 10.81	6 C carbon 12.01	
11 Na sodium 22.99	12 Mg magnesium 24.31															13 Al aluminum 26.98	14 Si silicon 28.09	
19 K potassium 39.10	20 Ca calcium 40.08	3B	4B	5B	6B	7B	8B		11B	12B	31 Ga gallium 69.72	32 Ge germanium 72.58						
37 Rb rubidium 85.47	38 Sr strontium 87.62	21 Sc scandium 44.96	22 Ti titanium 47.88	23 V vanadium 50.94	24 Cr chromium 52.00	25 Mn manganese 54.94	26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.39	49 In indium 114.8	50 Sn tin 118.7					
		39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4							

Alkaline-Earth Metal - Carbon Complexes

Utilize C_{60} as a model system

Be and Mg

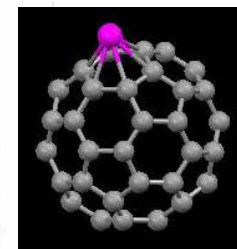
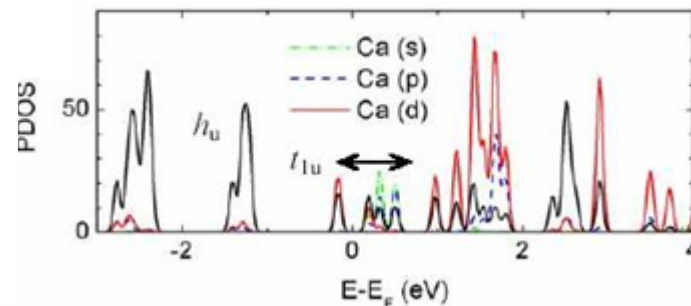
strong metal-carbon interactions via unique binding (empty d)



Be- C_{60} , Mg- C_{60}
 $\Delta E \sim 60 \text{ meV}$

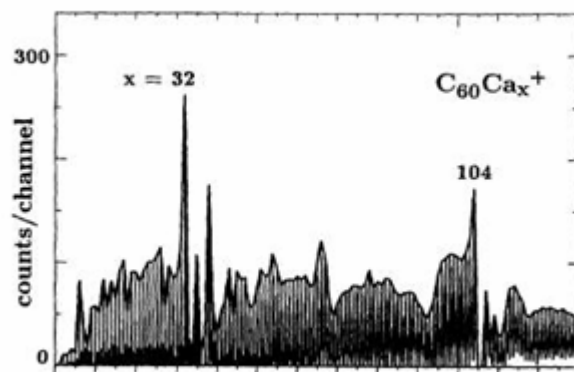
High ionization energy

Ca and Sr

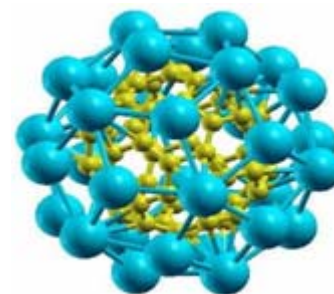


Ca- C_{60} , Sr- C_{60}
 $\Delta E \sim 1.3 \text{ eV}$

Low ionization energy



[Zimmermann et al.,
PRL **72**, 3542 (1994)]



$Ca_{32}C_{60}$, $Sr_{32}C_{60}$

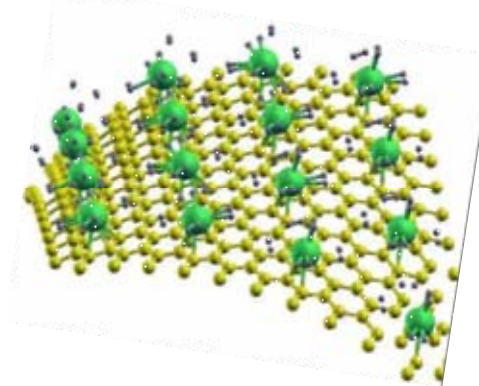
Ca and Sr are predicted to form uniform coatings on C, without clustering

Enhanced Hydrogen Binding to AEM-Coated Carbon Nanostructures

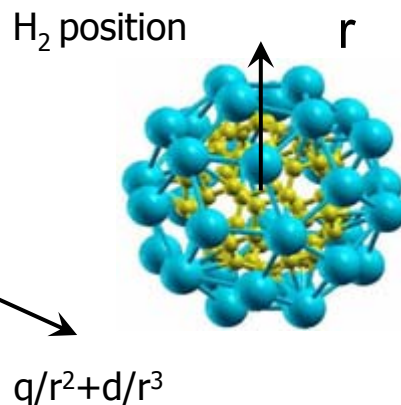
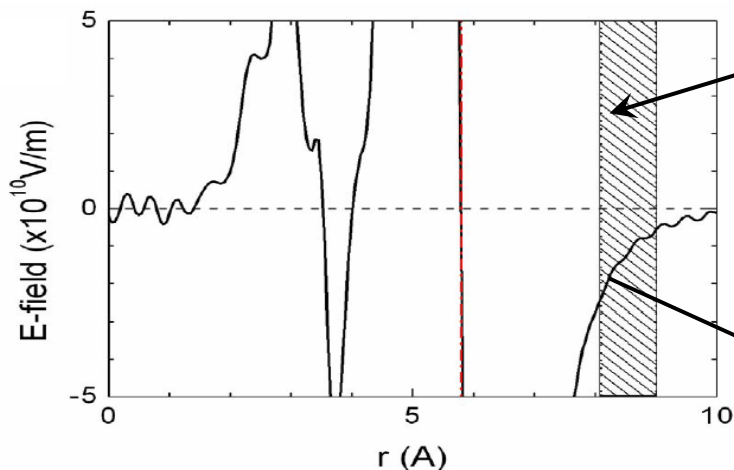
- Ca and Sr coated carbon nanostructures generate good H₂ binding sites:



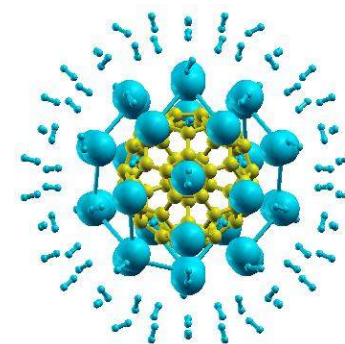
5H₂ per site:
 $\Delta E \sim 0.4\text{eV}$ per H₂



- High H₂ binding energy & High gravimetric density:



92H₂-Ca₃₂C₆₀ (8.4 wt%)



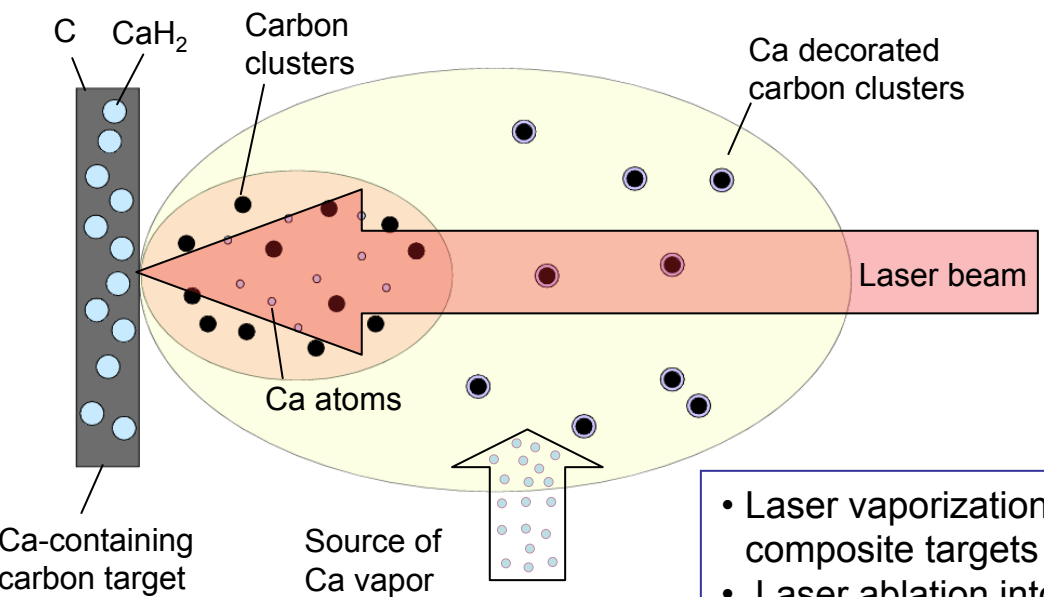
$\Delta E \sim 0.4\text{eV}/\text{H}_2$

cf) 92H₂-Sr₃₂C₆₀: 5.0 wt%

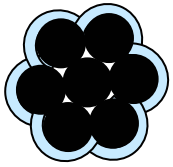
[M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang, Phys. Rev. Lett. (in press)]

Ca is superior to all the metal coating elements that have been studied

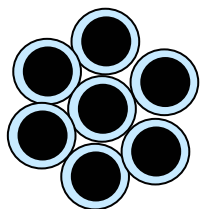
Ca-Decoration of SWNHs: Techniques Developed



Different scenarios for CNHs formation



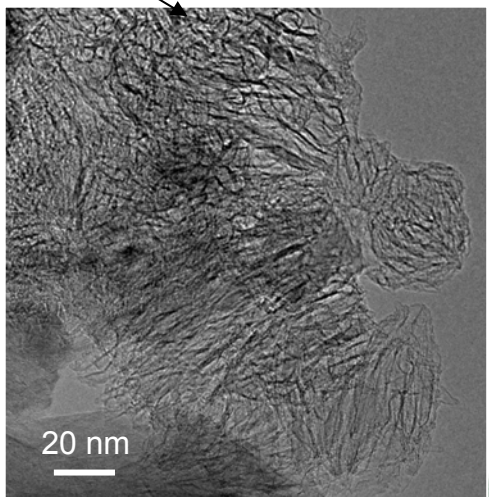
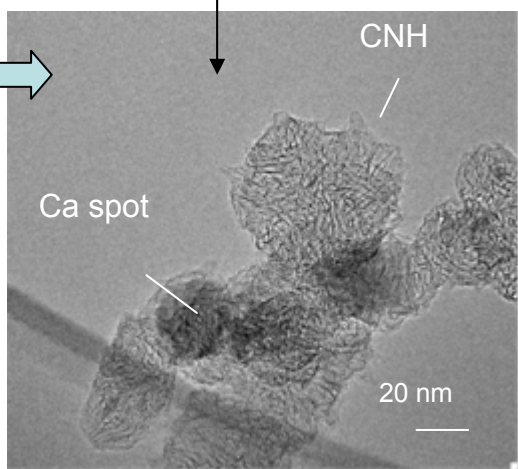
Aggregation of nanohorn units followed by Ca decoration



Ca decoration followed by decorated units aggregation

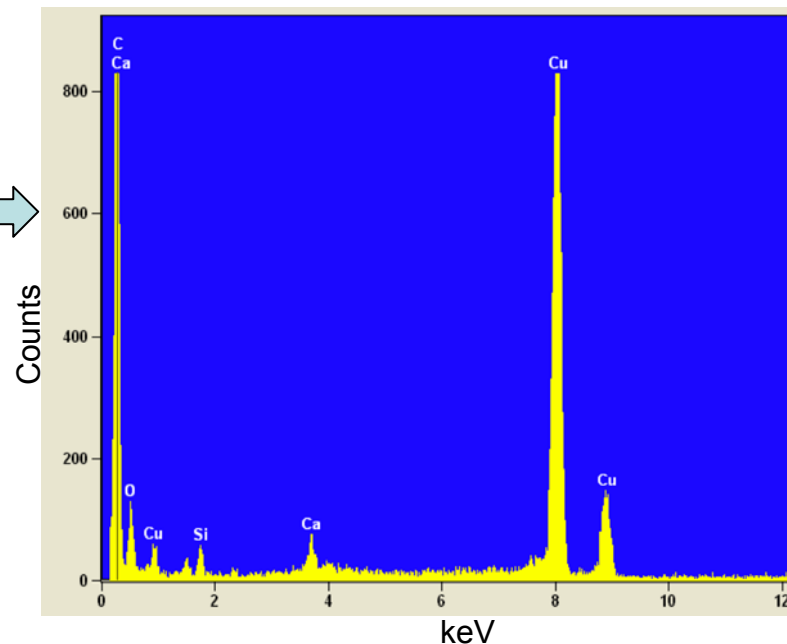
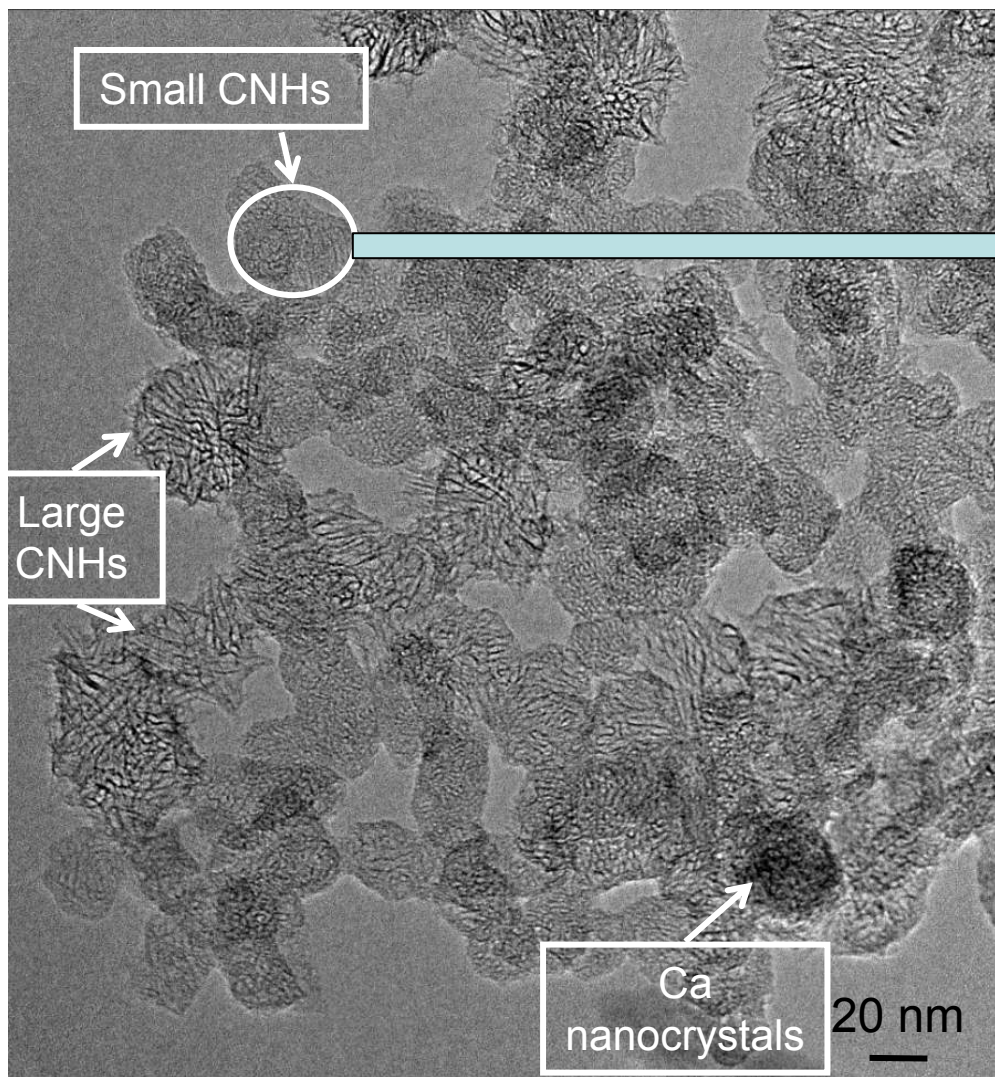
- Laser vaporization of C/CaH₂ composite targets
- Laser ablation into CaF₂ vapor
- Infiltration with atomic Ca vapor

- Ca-decorated SWNHs: TEM images**
- Layered, aligned structures
 - Homogeneous Ca-coated SWNHs
 - Ca infiltrates especially onto small nanohorns
 - Ca affects nanohorn formation - new structures
 - Large (20nm) Ca nc observed also.



Different techniques are being developed to synthesize Ca-doped CNHs

Energy Dispersive X-ray (EDX) analysis of Ca decorated carbon nanohorns by vapor infiltration

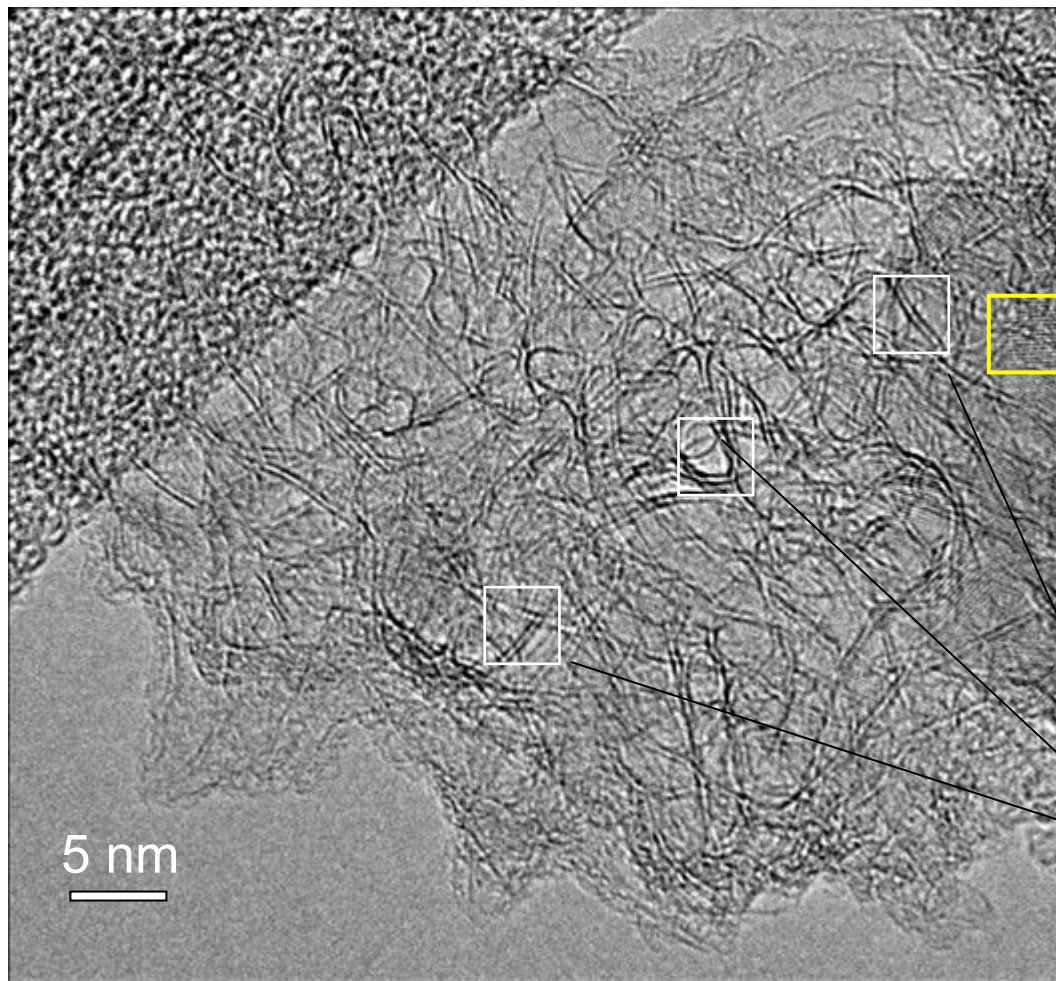


- Uniform Ca within SWNH aggregates
- Higher Ca abundance in “small” nanohorns compared to “large” ones
- Ca nanocrystals were observed

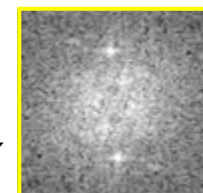
High resolution electron microscopy and EDX show presence of Ca in CNHs

Larger Graphene Spacing in Ca-Decorated SWNHs

High resolution TEM image of CNHs



FFT



- Average spacing, ~ 0.24 nm
- Indicates presence of Ca in these spots

- Average spacing, ~ 0.4 nm exceeds that in graphite, 0.34 nm
- Possible Ca intercalation

High resolution TEM images indicate possible interstitial Ca intercalation

Future Work

- **Focus on experimental verification of enhanced hydrogen sorption and binding energy using charged nanostructures and spillover:**
 - **Ca-decorated SWNHs:** Improve decoration and characterization techniques
 - Decoration: *In situ* decoration preferable, utilize graphene structures?
 - Characterization: HRTEM and EDX, Z-STEM and EELS to assess uniformity of coating, dispersal
 - NMR, neutron scattering, sorption studies - gram quantities- **MILESTONE 9/08**
 - **Elegant surface science experiments with charged nanostructures**
 - **Theoretical calculations of alternate structures with large dipole moments and optimal pore sizes (see supplementary slides) **MILESTONE 9/08****
- **Understand cluster formation processes for transition metals on C **MILESTONE 6/08****
 - *Developing a theoretical understanding of the spillover mechanism*
 - **Understanding hydrogen dynamics at the interface between support materials (nanohorns) and catalyst particles**
 - **The goal is to find a way to increase hydrogen kinetics during spillover process**
 - **Theoretically designed system will be tested experimentally using metal-coated nanohorns**
- **Increase surface areas and develop decoration techniques of nanocarbon materials:**
 - **Experiment with SWNH and C-np aerogel composites. **MILESTONE 6/08****
 - **Experiment also with graphene synthesized by laser vaporization (see supplementary slides)**
 - **And aligned large-diameter VANTAs which are decorable and tailorable (see suppl. slides)**

Summary

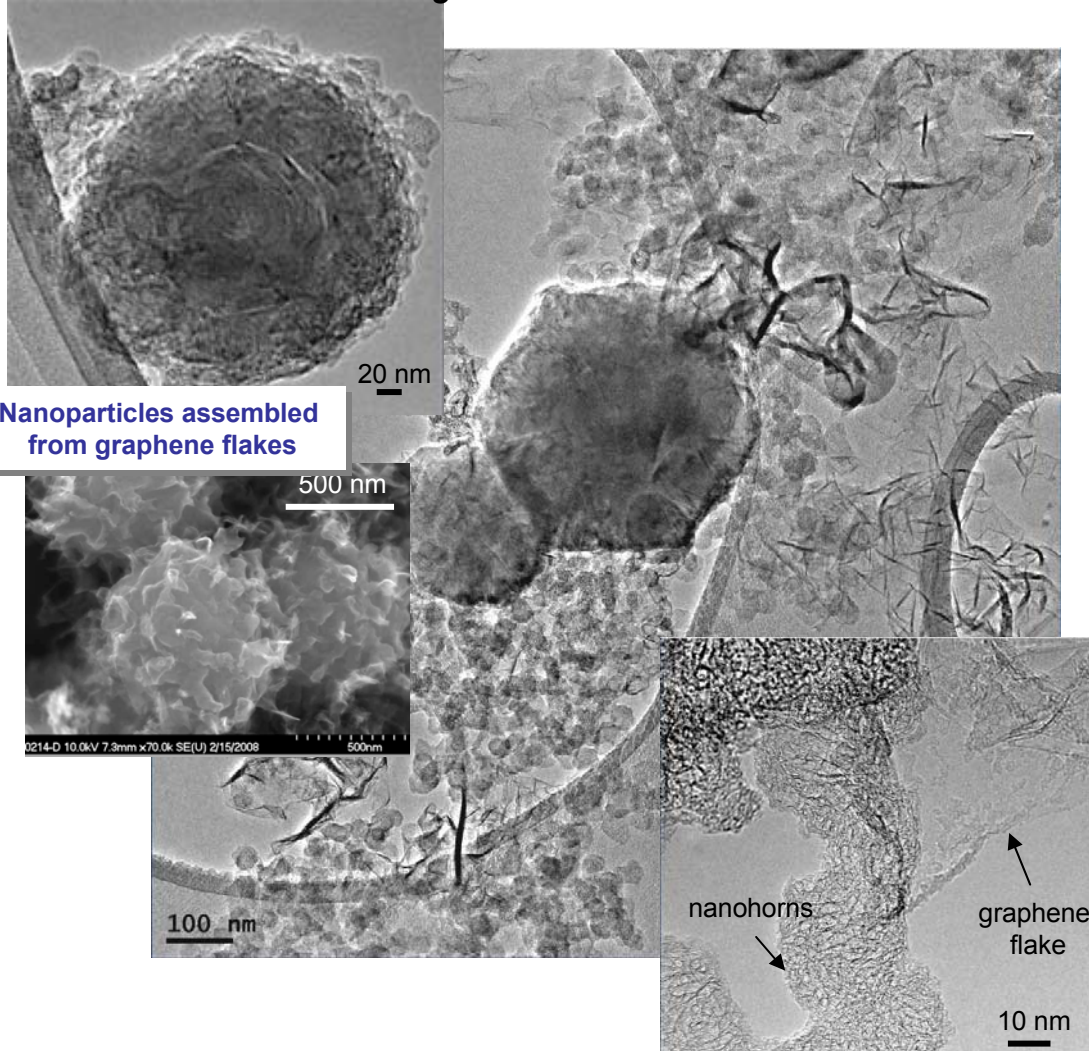
- **Overall:** Metal-decorated, activated carbon nanohorns are promising candidates for nanoengineered hydrogen storage media with enhanced binding energy. Tunable pore sizes have been achieved during synthesis and processing, and metal decoration leads to enhanced binding energies.
- **Nanohorns: Synthesis and Processing:**
 - *High surface areas:* SWNHs were synthesized in gram quantities with pore sizes adjusted to maximize surface area (2142 m²/g) and increase excess storage (3.5 wt. % at 77K).
 - *Tunable, small pores:* NMR confirmed the majority of storage in the interstitial pores on large SWNHs, and in activated pores (< 1 nm) in short-SWNHs.
 - *Room temperature storage:* Undecorated, short O-SWNHs reversibly store significant hydrogen (0.6 wt.% at 30 bar) at room temperature, comparable to bridged MOFs and Pt-decorated O-SWNHs (1.5 wt.% at 100 bar). Mechanism unclear.
 - Variable graphitic structures possible by altering synthesis conditions (including graphene flakes).
- **Understanding Mechanisms:**
 - Upon metal decoration by Pt and Pd clusters, SWNHs exhibit enhanced binding energy and evidence of storage due to spillover.
 - A theoretical analysis was performed to understand the mechanism for the enhanced binding energy, and *electric dipole-induced storage* was proposed.
 - A theoretical search for new nanostructures with stable dipole fields was begun. Several new systems identified, including organic molecule-based structures.
 - From the search, of all the elements, alkaline earth metals **Ca and Sr** were predicted to have a special ability to coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H₂ with **8.4 wt. % and 0.4 eV** for Ca.
 - Several methods have been developed to produce Ca-decorated SWNHs, and a simple method of vapor phase infiltration so far appears to be the most effective.
- **Program Focus:** Testing predictions of enhanced binding energy and storage in metal-decorated nanohorns using high permanent electric fields and optimal pore sizes.

Summary Table

Different types of nanohorns		Surface area, BET (m ² /g)	Pore size (nm)	H ₂ uptake at 300K (wt.%)	H ₂ uptake at 100K (wt.%)	H ₂ uptake at 77K (wt.%)	H ₂ uptake at 30K (wt.%)
As prepared "long"	AP-SWNHs	453		0.18 (AirProd.) 0.2 (NIST)	0.6 (NIST)	1.0 (NREL) 0.8 (NIST)	1.7 (NIST)
Opened by oxidation "long"	O-SWNHs-4	1191	1.5(BET)				
	O-SWNHs-3	1590	1.7(BET)			2.5(30bar) (CalTech)	
	O-SWNHs-5	1892	1.7(BET)				
As prepared, Pt dec., "long"	SWNH/Pt-LA			0.22 (AirProd.) 0.2 (NIST)	0.6 (NIST)	1.0 (NREL) 0.8 (NIST)	1.7 (NIST)
	SWNH/Pt-CH			0.28 (110bar) (AirProducts)			
Opened and Pt dec., "long"	O-SWNH-3/Pt-CH					2.2(30bar) (CalTech)	
				1.5 (100bar) (UNC)			
Opened, "short"	O-SWNHs_1	2142		0.6 (30bar) NIST	2.7 (30bar) NIST	3.5 (25bar) NIST	6.3 (4bar) NIST
Opened "short"	O-SWNHs_2		≤1(NMR) (UNC)				

Future Work Tailoring carbon nanostructures for enhanced hydrogen storage: graphene flakes and graphite nanoparticles

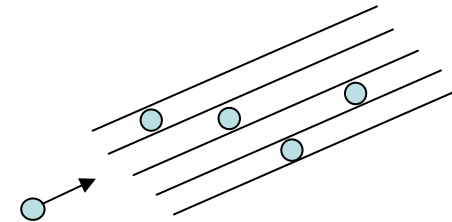
TEM and SEM images of new carbon nanostructures



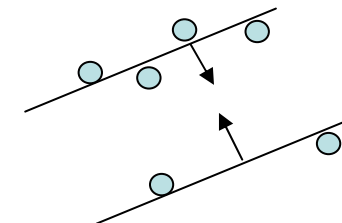
Nanoparticles assembled from graphene flakes

Different approaches for synthesis optimal hydrogen storage materials

- Intercalation of graphitic nanoparticles with metal atoms



- Decoration of graphene flakes with metal nanoparticles followed by assembly into layered nanoparticles.



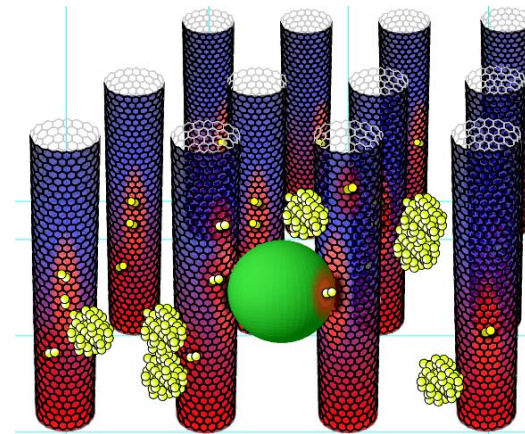
Graphene flakes and assembled nanoparticles were made by laser vaporization in H₂, providing further opportunities to decorate nanomaterials for enhanced hydrogen storage.

Future Work

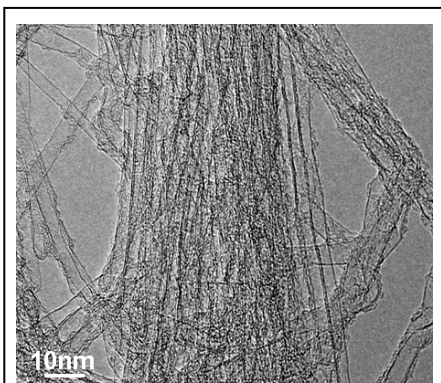
Nanohorn Composites for Faster Loading and Thermal Management

Vertically Aligned Nano-Tube Arrays - VANTAs -

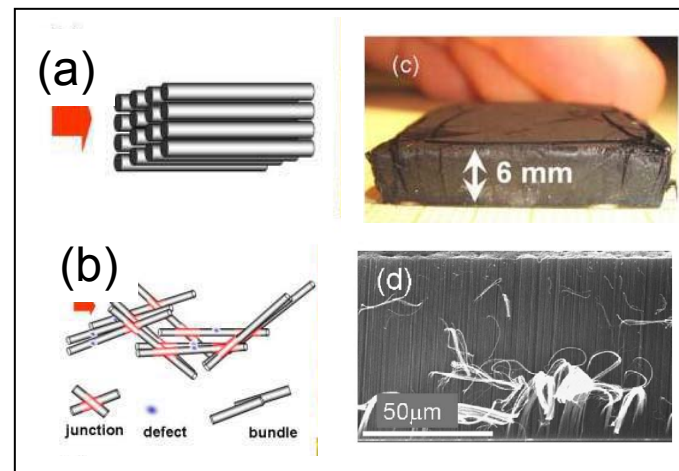
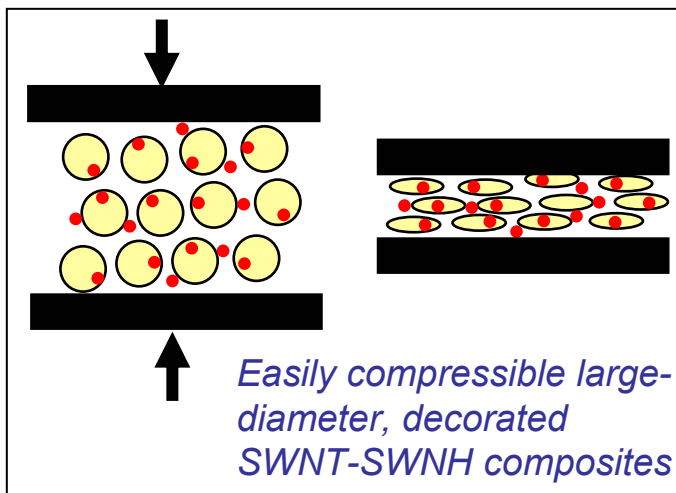
- Have been synthesized as compressible large-diameter single-walls at ORNL in multi-millimeter long bulk composites
- Have thermal conductivities which outperform any other macroscopic nanotube assembly, and are currently a factor of 3 better than currently used thermal interface materials
 - 15 ± 2 W/mK for 8 vol. % MWNT,
 - Up to 72:1 anisotropy in thermal diffusivity longitudinal:transverse



CONCEPT: Use decoration techniques and pore size optimization established for SWNHs to tailor composites with these materials to provide simultaneous storage and high thermal conductivity



Large diameter SWNT-VANTAs



I. N. Ivanov, et al., *Appl. Phys. Lett.* **89**, 223110 (2006).

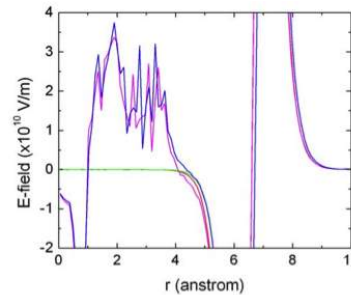
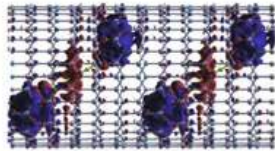
Future Work

Designing nanostructures with high electric fields to polarize and store H₂

- How do we design a structure which can produce a static electric field in a charge compensated way?

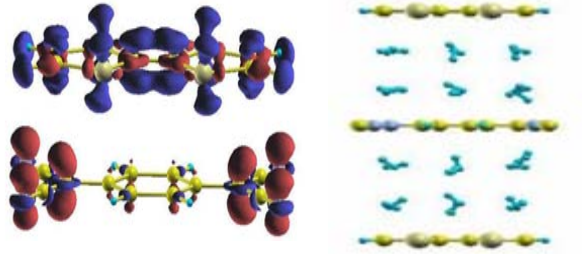
Example:

High electric field inside a NT



Organic molecules inside nanostructures can generate sufficient E-fields for H₂ storage (e.g. TCNQ @ (17,0) SWNT)
[M. Yoon (to be submitted)]

Example:



TTF-TCNQ

$\Delta E \sim 0.2 \text{ eV/H}_2$, >10 wt%

[M. Yoon (to be submitted)]

Charge compensated structures exist in nature, and can be synthesized