Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

DOE Hydrogen Program

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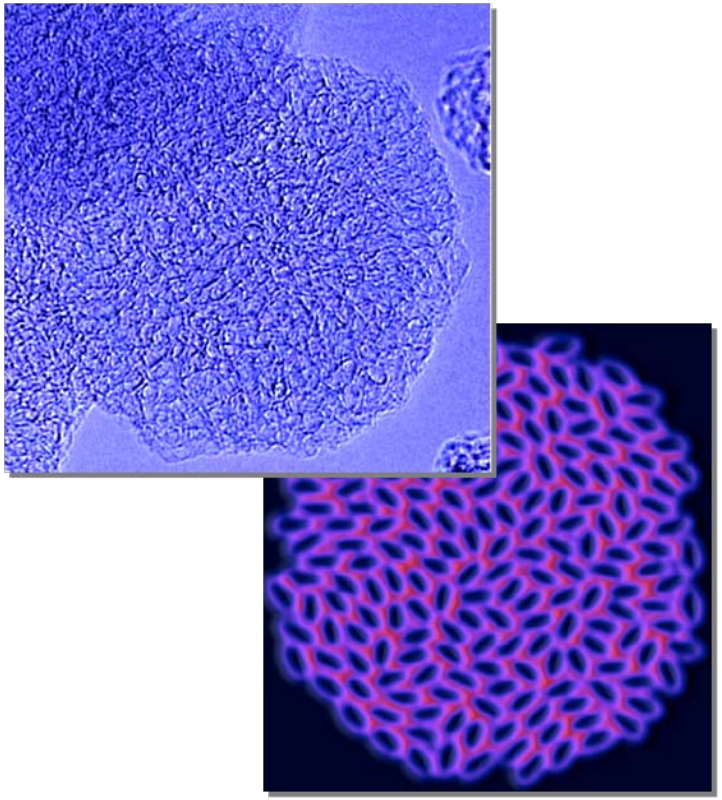

Project ID STP_26_Geohegan

DOE Hydrogen Program Annual Merit Review, May 20, 2009

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Overview

Timeline

- Project start date: FY05
- Project end date: Jan 2010
- 85% complete

Budget

- Total project funding
  - DOE share 1.6 M$
  - Contractor share 0k
- 440k received in FY09

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
  - Rice Univ. - Charged Engineered Nanospaces

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Objectives

Overall

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

- Carbon nanohorns are hollow single-walled nanostructures which form unique aggregates. Their pores have been tuned in this project to sub-nm sizes. In this project we have shown that:
  1) Metal-free SWNHs possess unique storage sites which store up to 0.6 wt.% H_2 at RT (30 bar).
  2) Metal-decorated SWNHs exhibit clear spillover, enabling up to 1.5 wt.% H_2 storage at RT (100 bar).
  3) Ca-decorated SWNHs are theoretically predicted to be the optimal metal-coated carbon hybrid nanostructure - exhibiting uniform coatings and enhanced uptake (theoretical 8.4 wt.% H_2 at RT) - an example of a new ***charged nanostructure.***

2009

- The objectives for 2009 are to concentrate on
  - Developing activation processes to nanoengineer sub-nm pores in SWNHs with high binding energy
  - Developing new techniques to Ca-decorate opened SWNHs to test the theoretical predictions of enhanced uptake, smooth coatings.
  - To computationally address hydrogen storage in metal-decorated carbons, such as Ca-O-SWNHs, and other ***charged nanostructures*** which are designed with high static electric fields in nanoengineered pores or layers.

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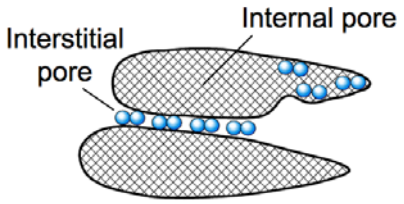
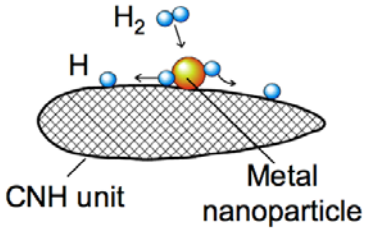
Approach

Bottom-up synthesis approach:

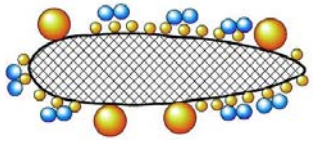
- **Tune the shape of individual nanohorns during synthesis to find morphologies with adsorption sites & high binding energy (e.g. in tips of SWNHs)**
- **These nanohorns form aggregates with interstitial pores. Activate these aggregates to tune the interstitial pores and access the internal pores.**
- **Metal-decorate these activated aggregates for spillover-based storage or strong binding directly on the metal coating.**



Engineered Nanospaces



Spillover from Metals



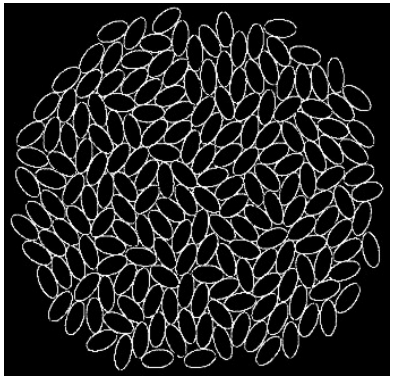
Strong Binding of H_2 on Metals

This approach permits the benefits of storage in engineered nanospaces and that from metal-induced storage to be explored and tuned separately

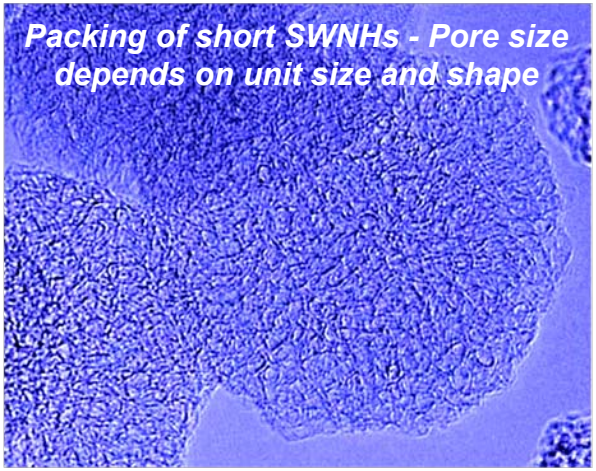
2009: Concentrate on Ca-decorated, short SWNHs

Why?

1) Short SWNHs assemble into aggregates with sub-nm pores and show RT storage *without* metal.
2) Ca-decoration is predicted to form a uniform coating on C which should have high electric fields to polarize hydrogen and increase binding energy



Graphic:*www.physics.nyu.edu /~pc86/packing.html*



New focus on charged nanostructures.

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Milestones and Tasks

Task 1: Defect and space engineering of nanohorns

1.1 Theory: Theoretical studies for the optimum morphology of nanohorns for hydrogen storage (3/09) and the role of defects in functionalizing nanohorns (6/09)

1.2 Expt: Experimental study on the activation process, to understand how both internal pore volume and interstitial pore volume can be simultaneously tuned (6/09)

Milestones Achieved / In Progress

- *Energy stability calculations performed for different carbon nanostructure morphologies incorporating hydrogen vs. defect density.*
- *Pore defects simulations including oxygen decoration in progress*
- *New organic charged nanostructures surveyed*

Milestone Achieved / in Progress

- *NMR results (UNC) reveal new small interstitial pores store significant hydrogen in long SWNHs.*
- *KOH activation performed.*
- *New apparatus built and implemented for more uniform gas-phase oxidation and in situ hydrogen sorption testing.*

Task 2: Calcium-decorated nanohorns: Cyclability and optimum coating

2.1 Theory: study of hydrogen storage capacities of inside and outside Ca-decorated nanohorns (3/09) and possible chemical reactions near defect sites (9/09)

2.2 Expt: Synthesis of Ca-decorated SWNHs under different experimental methodologies, delivery of 100mg quantites of as-processed and decorated SWNHs to partners (6/09)

Milestone Achieved / In Progress

- *Metal cluster stabilities and hydrogen uptakes calculated including the role of charge on curved C nanostructures*
- *Defect site local charge density effects on dipole moments for hydrogen polarization underway*

Milestone Achieved / In Progress

Laser decoration and vapor-phase infiltration techniques for Ca-decoration performed and evaluated. 100 mg samples delivered to partners. AX-21 also introduced as standard material. Further modifications necessary and in progress.

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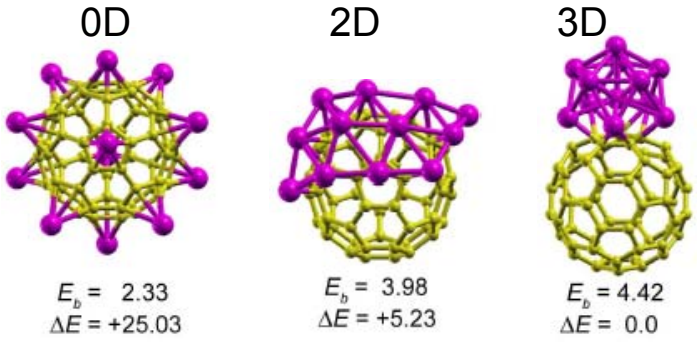
Technical Accomplishment

Understanding transition metal interactions with nanocarbons for metal coatings and designed spillover materials

Ti atom interaction with C_{60}

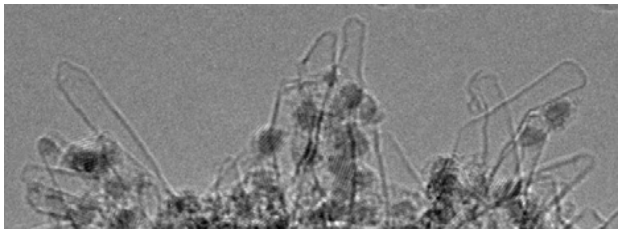


Energetically, cluster formation is always favorable for a cluster of $N>N_C$: (example: N_C=5 for Ti)

-$N<N_C$, 2D is more favorable
-$N>N_C$, 3D is more favorable

Relative stabilities between different metal configurations on nanocarbon surfaces are compared

[S. Yang, M. Yoon, et al.
J. Chem Phys. 129, 134707 (2008)]
*Also see: Sun et al. JACS, **127**, 14582(2005)*



TEM images shows the formation of transition metal (Pd) clusters on nanohorn surfaces. Energetically, cluster formation is much more favorable due to metals' high cohesive energy.

Energy calculations have been performed to predict the morphology of different metals on C supports

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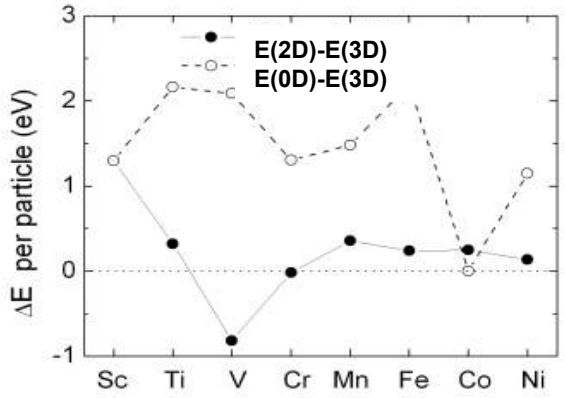
Understanding transition metal interactions with nanocarbons for metal coatings and designed spillover materials *(continued)*

- C_{60} interaction with other 3*d*-transition metals

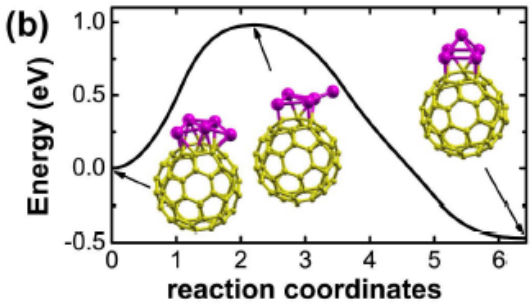


Relative stabilities between different morphologies (0D, 2D, and 3D) are different for each transition metal. Theory predicts that V, for example, can be easily stabilized against clustering .

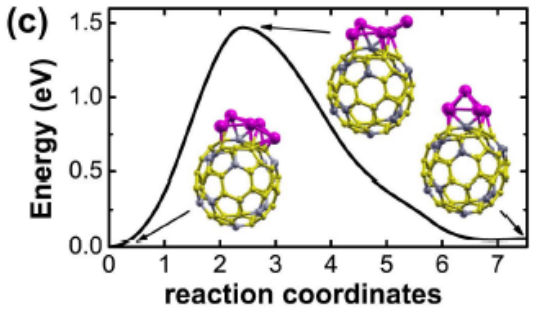
[M. Yoon (to be submitted)]

- B-doping helps to prevent the metal clustering:

Kinetic barrier for 3D cluster formation can be higher by 50% by Boron doping



No Boron doping



With Boron doping

[S. Yang, M. Yoon, E. Wang, Z. Zhang, J. Chem Phys. 129, 134707 (2008)]

Experimental confirmation: Homogeneous Pt doping on B-doped C

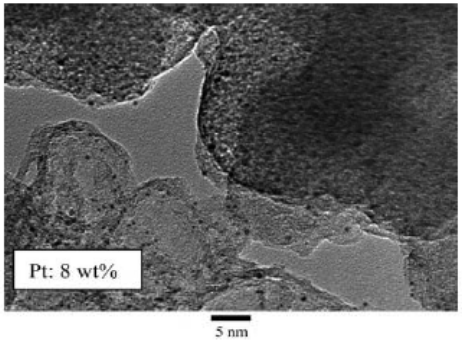


FIGURE 3. TEM Micrographs of Pt/B/C Materials Prepared by Doping with H_2PtCl_6 (top) with Surfactant and (bottom) without Surfactant

[M. Chung et al, Penn. State, Univ.]

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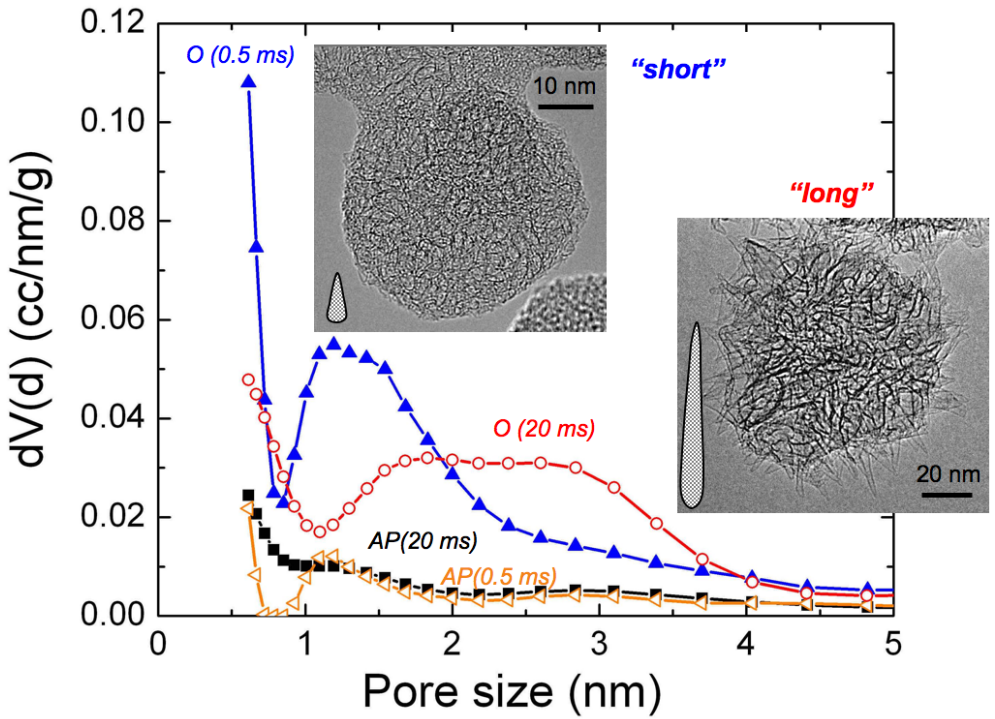
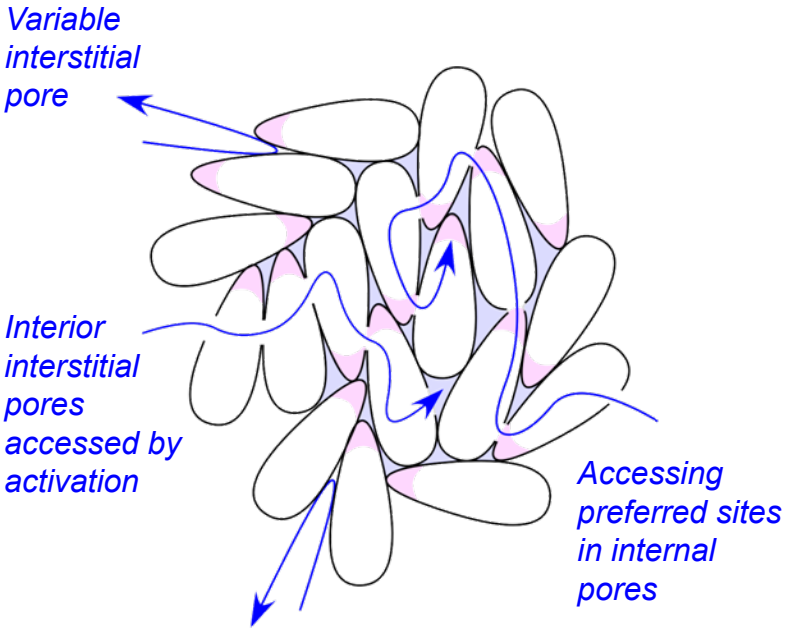
Tuning pore sizes during synthesis and processing



Tuning internal pore size during synthesis



Aggregates have unique internal and interstitial pore sizes - tuned by activation

As-produced (AP) and oxidized (O) nanohorn aggregates have been synthesized using different laser pulse widths, resulting in "short" and "long" individual structures and their aggregates. The internal pore (left) was tuned to enhance the formation of preferred "tip" sites (pink), and the aggregate packing resulted in desirable sub-nm interstitial pores (blue) which are accessed by oxidative activation (see NMR data for impact on hydrogen storage).

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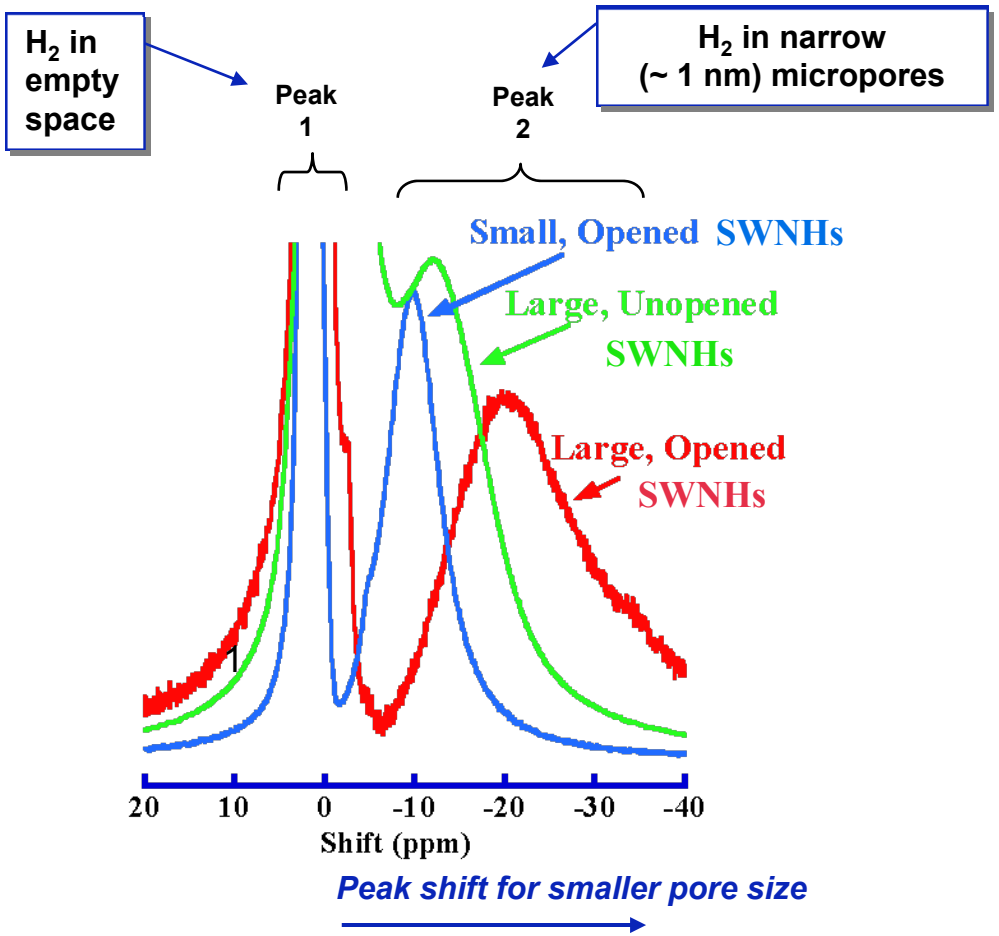
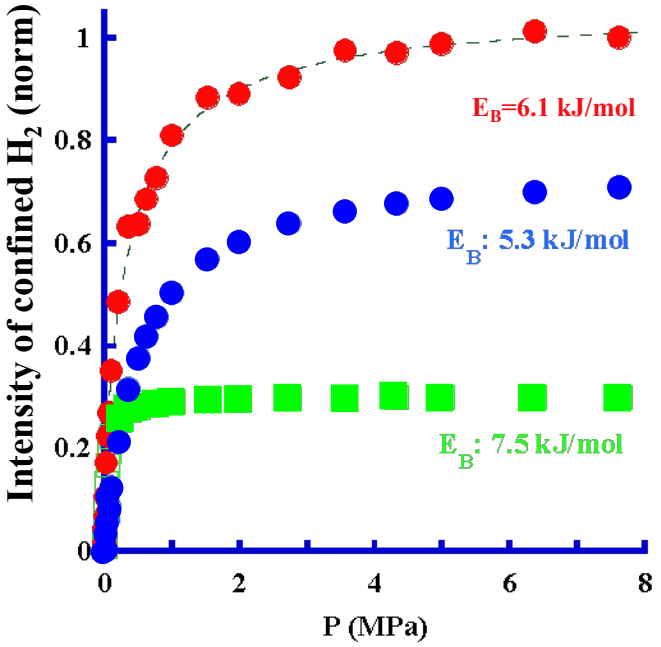
Technical Accomplishment

NMR Measurements of Adsorbed Hydrogen in Sub-nanometer Pores of SWNHs – *by UNC*





Large opened nanohorns show the largest NMR shift for among all nanoporous materials studied at UNC, indicating storage of hydrogen in small (sub-nm) pores suitable for enhanced adsorption.

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See poster STP 28 Wu for details

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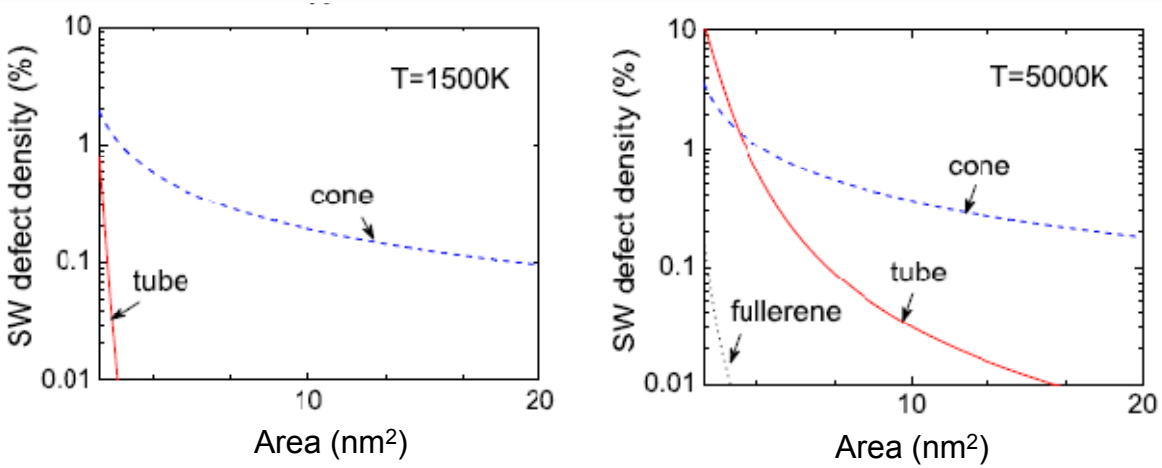
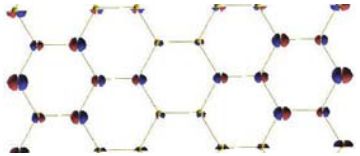
Tailoring carbon nanostructures & defect engineering for enhanced hydrogen storage: Theoretical predictions



Defect engineering: Predicting defect density of different carbon morphologies at different temperatures (T) & nanostructure size (surface area).
Theory predicts that highly curved structures (for example small size of nanohorn aggregates) can contain significantly large amounts of defects due to entropic effects. The created defects can be used as reaction centers for H_2 adsorption as shown below as an example:

Defects can capture local charge densities, thus H_2 binding can be enhanced



The stability of different nanostructures synthesized at different temperatures has been theoretically predicted to understand the defect densities relevant for enhanced hydrogen binding energy.

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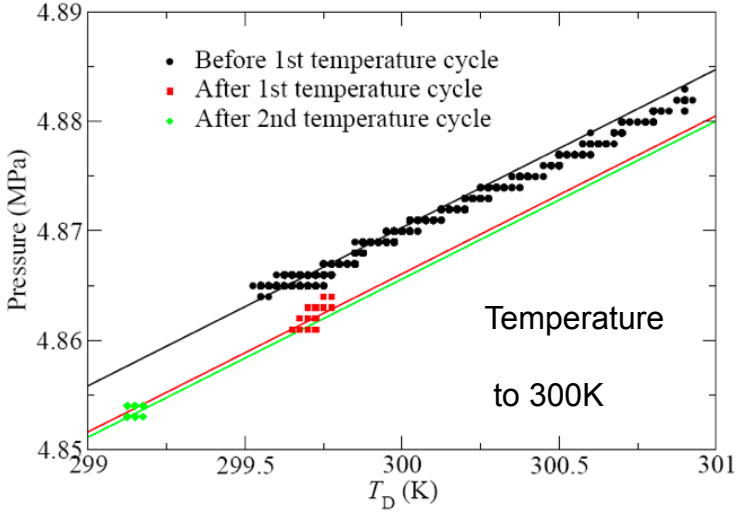
Technical Accomplishment

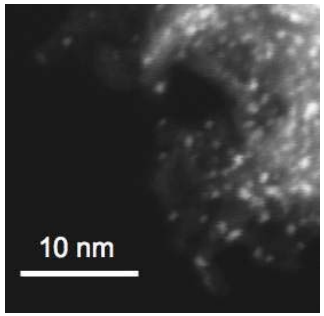
Pt-decorated "long" opened SWNHs show spillover effect

NIST

Pressure difference measurements by NIST

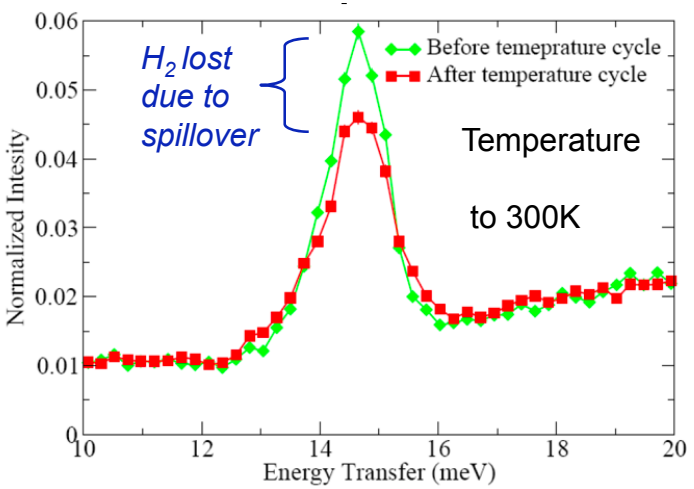


O-SWNHs/Pt



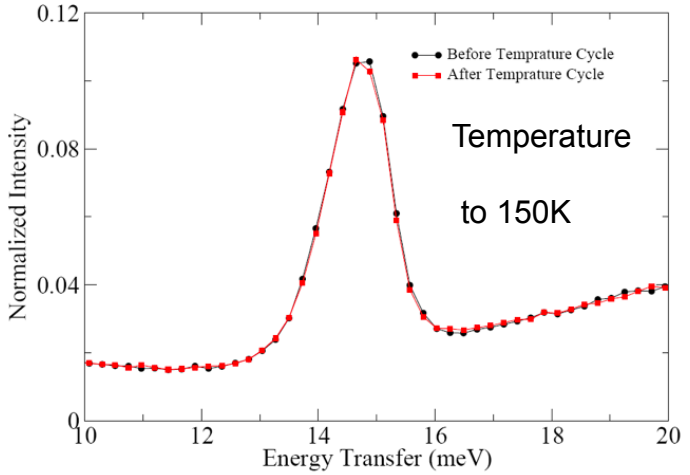
Z-STEM of sample

Neutron scattering measurements by NIST



Pressure measurements confirm neutron scattering results

- "Spillover" measurements confirm that Pt-decorated SWNHs dissociate H_2 with an onset temperature between 150K < T < 298K.
- Pt-decorated SWNHs showed the clearest evidence for the spillover effect among all other materials studied at NIST.



Spillover plays a major role in hydrogen storage at room temperature in O-SWNHs/Pt.

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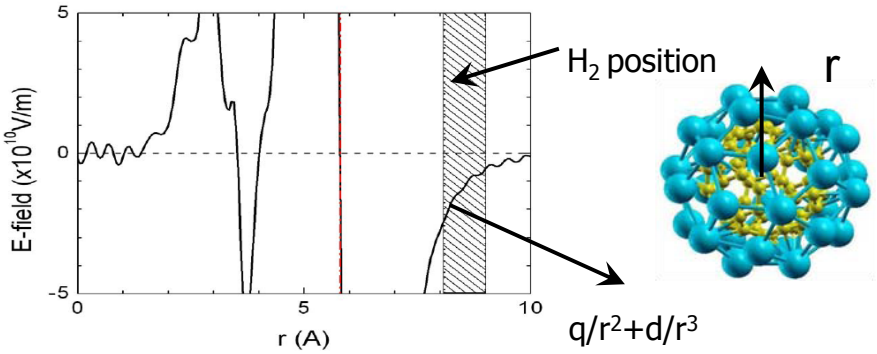
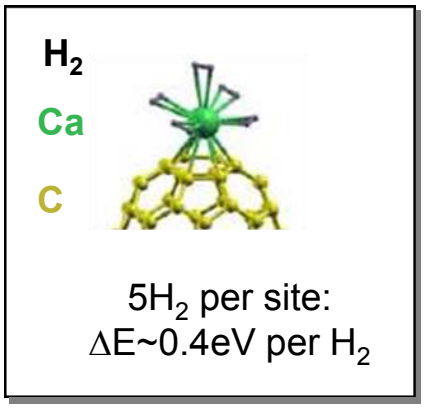
Technical Accomplishment

Enhanced Hydrogen Binding to Alkaline Earth Metal-Coated Carbon Nanostructures

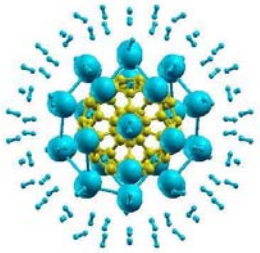
- **Ca and Sr coated carbon nanostructures generate good H_2 binding sites:**



High electric fields sufficient to bind hydrogen by induced polarization are produced very near the Ca-carbon surface

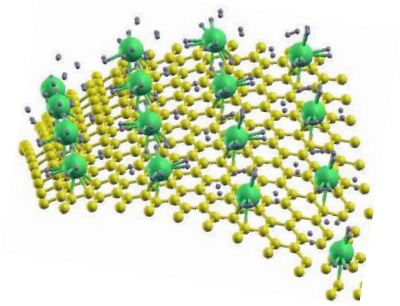


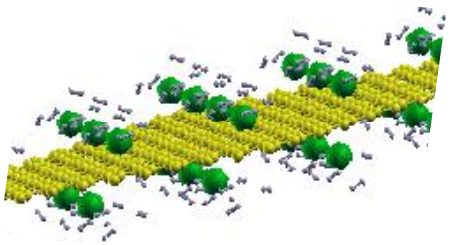
- **High H_2 binding energy & High gravimetric density: 8.4 wt.% on curved or flat graphene**



$92H_2$-$Ca_{32}C_{60}$ (8.4 wt%)[1]

$\Delta E \sim 0.4 eV/H_2$





Ca can stably decorate both sides of nanocarbons
-> high H-capacity can be achieved

Theory predicts that alkaline earth metals Ca and Sr uniformly coat C nanostructures and result in high electric fields which should bind high quantities of hydrogen. Can these be experimentally verified?

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[1][M. Yoon et al. Phys. Rev. Lett. (2008)] 32 Ca on one-side of C_{60}

[2][C. Ataca et al. Phys. Rev. B. (2009)] 2 Ca on both sides of 2x2 graphene.

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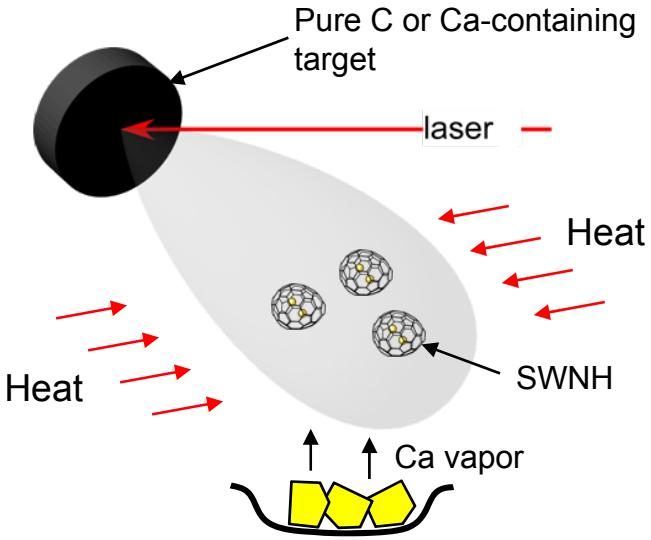
Developing scalable strategies for Ca decoration of nanocarbons



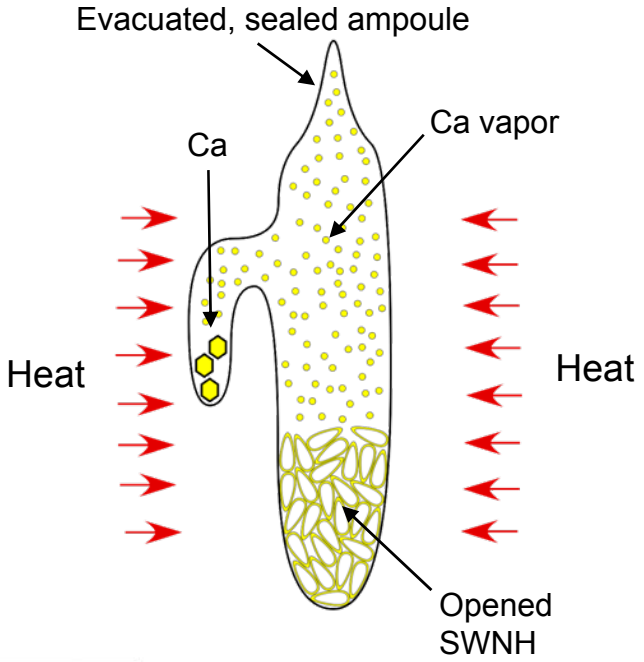
Three techniques developed

→ in situ

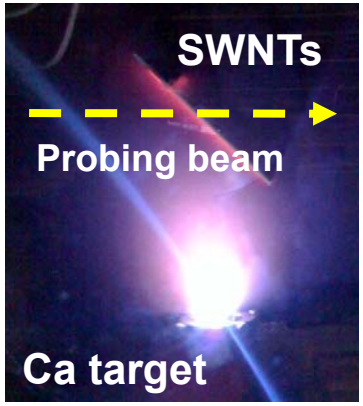
- LV of composite target
- LV of pure target in Ca vapor

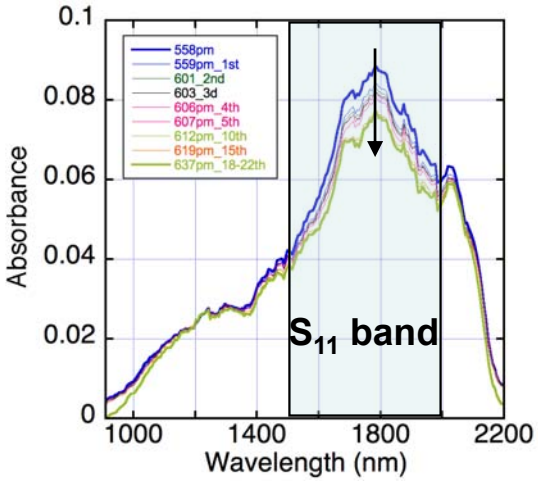
→ ex situ

- Activation followed by metal vapor infiltration



In situ spectroscopy supports theoretical predictions - Ca charge transfer to C observed via decrease in S_{11} band strength





Different techniques were developed to decorate C nanostructures with Ca and confirm the existence of charge transfer

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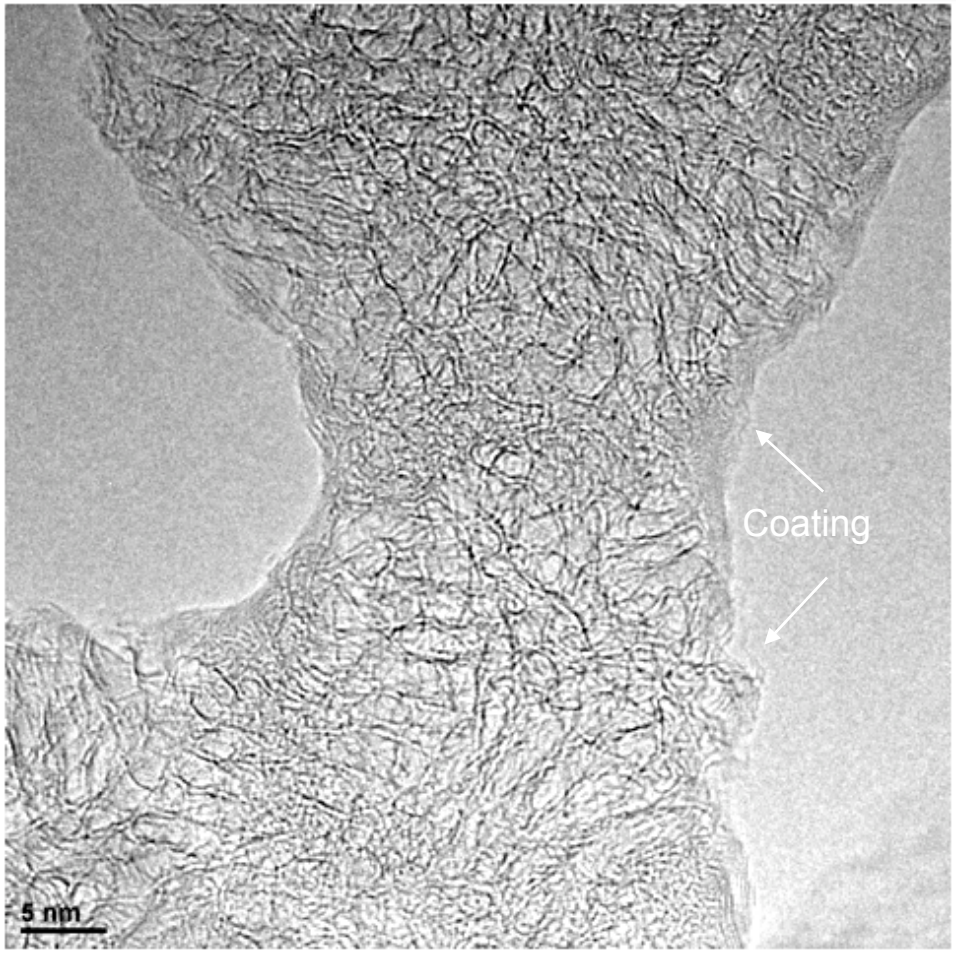
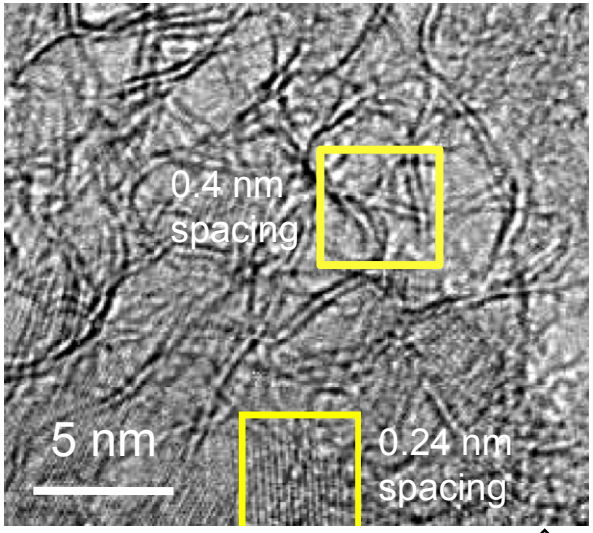
Technical Accomplishment

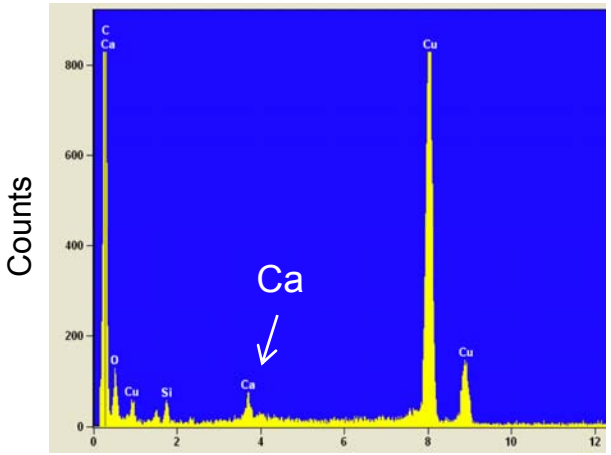
High resolution TEM analysis of Ca-decorated carbon nanohorns produced by vapor infiltration



High resolution TEM image of CNHs



Average spacing of 0.24 and 0.4 nm was found in high resolution TEM images



EDX spectrum

High resolution electron microscopy and EDX show Ca present in CNHs and smoothly coated surfaces

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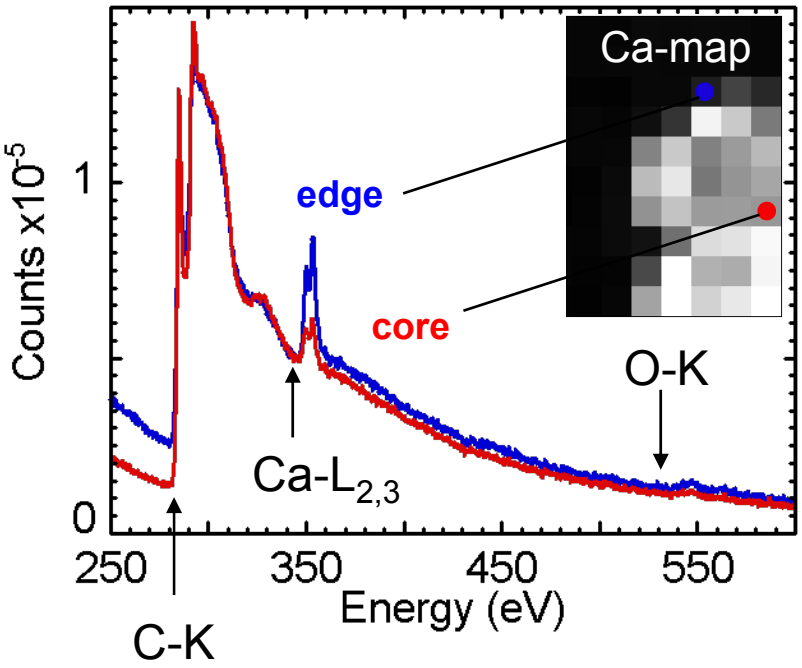
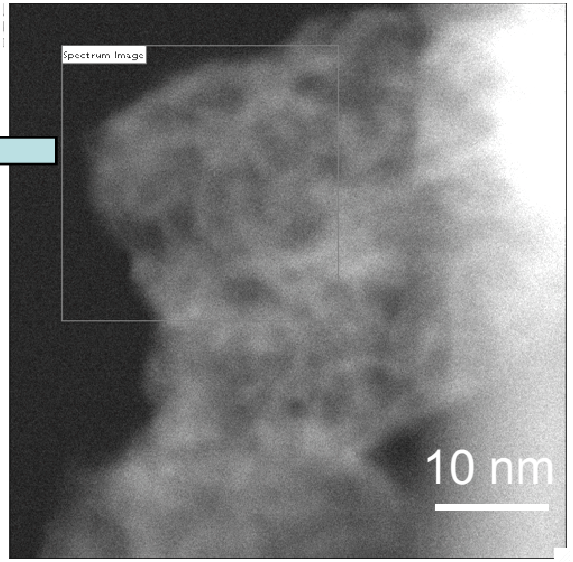
Nanoparticle-free Ca decoration of carbon nanohorns: AC-Z-STEM and EELS analysis

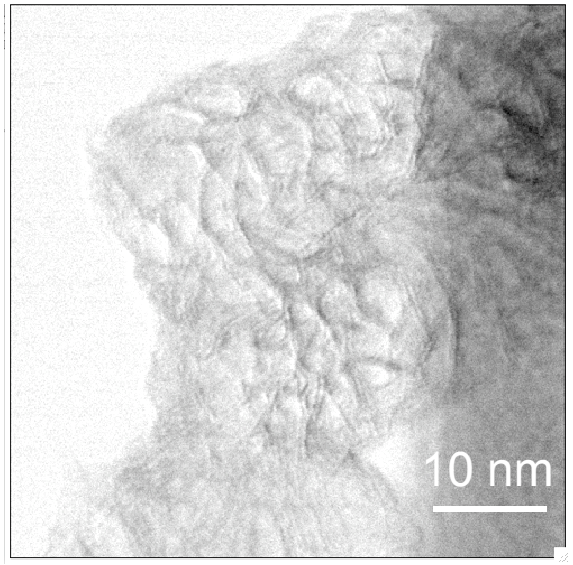
EELS spectra of Ca-decorated nanohorns



Dark and bright STEM images Of Ca-decorated nanohorns



Z-Contrast Image shows uniformly distributed Ca on SWNHs



Bright field STEM image (< 2Å beam).

Z-STEM imaging and EELS mapping shows relatively uniform, nanoparticle-free Ca-decoration of nanohorns on the nm scale in accordance with theoretical predictions

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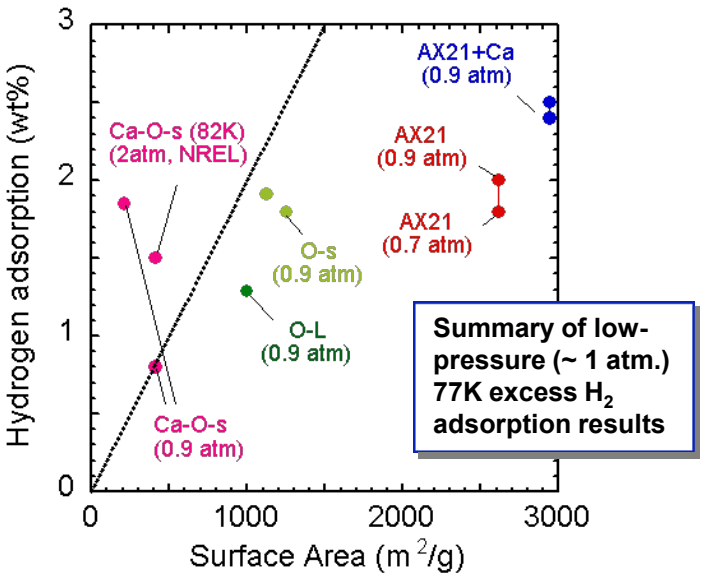
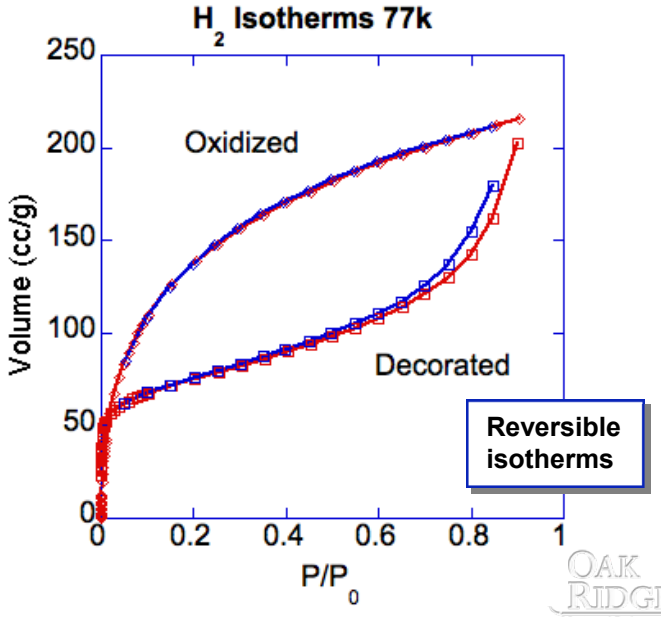
Technical Accomplishment

Low pressure excess hydrogen adsorption in Ca-Decorated carbon nanostructures materials at 77K: SWNHs and AX21

Material	H_2 wt%	@ P (atm) H_2	N_2 BET surface area (m^2/g)	FOM (H_2 wt% per 500 m^2/g per atm H_2
S-O-SWNHs +Ca (1)	1.85	0.9	212	4.8
S-O-SWNHs +Ca (2)	0.8	0.9	413	1.1
S-O-SWNHs (1)	1.9	0.9	1123	0.94
S-O-SWNHs +Ca (2)	1.5	2	413	0.91
S-O-SWNHs (2)	1.8	0.9	1251	0.80
L-O-SWNHs	1.3	0.9	997	0.72
AX21	1.8	0.7	2615	0.49
AX21+Ca	2.5	0.9	2942	0.47
AX21+Ca	2.4	0.9	2942	0.45
AX21	2	0.9	2615	0.42



- Ca-decoration of oxidized short SWNHs and AX-21 activated carbon were performed by high-temperature vapor infiltration in vacuum, and compared to undecorated samples.
- Although pore-blocking was observed by nitrogen BET, the hydrogen storage capacities at ~ 1 atm. in Ca-decorated samples already exceed those expected by Chahine's rule (see graph at right, and Figure of Merit (FOM) above).
- Interesting, reversible hydrogen isotherms at 77k (right) indicate possible capillary filling



Ca decoration results in clear enhancement of hydrogen adsorption even at highly reduced surface areas. The decoration process should be improved to preserve the surface area of nanostructured carbon.

AX-21 Courtesy of CalTech

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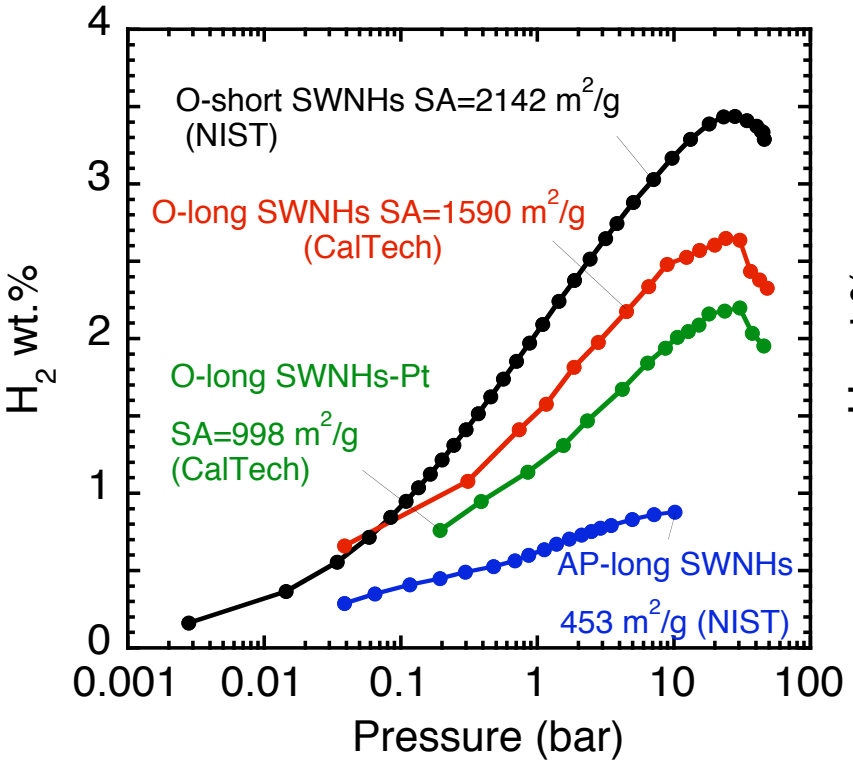
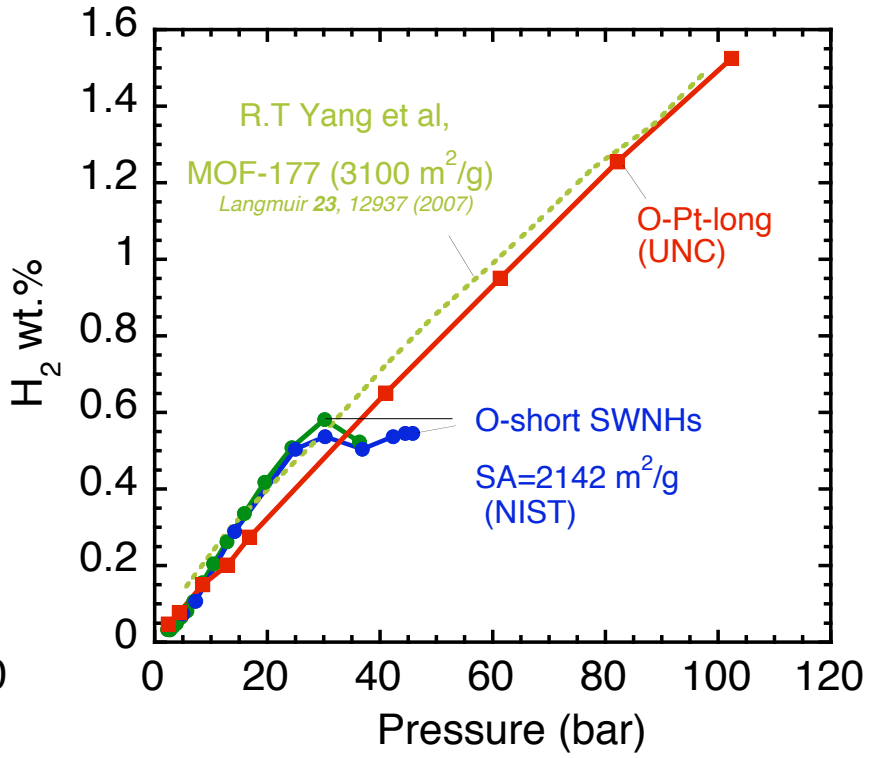
Nanoengineering of carbon nanohorns: pores in short oxidized SWNHs adsorb higher excess H_2

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 , and decorated long O-SWNHs exhibit significant RT uptake at higher pressures

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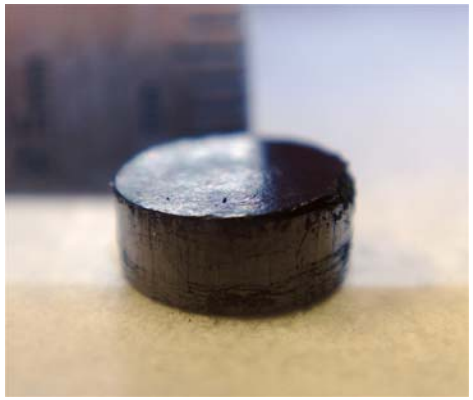
SWNHs: net gravimetric and volumetric capacities

Volumetric capacity

Volumetric capacities of 36 g/L (assuming 3.5 wt.% H_2 stored) were achieved in pure SWNHs which have been compressed to form dense pellets (1.03 g/cm^3).



SWNHs pressed pellet

Ca-decorated SWNHs with 8.4 wt.% H_2 stored should enable 86.4 g/L volumetric capacities to address 2010 (45 g/L) and 2015 (81 g/L) system targets.

Net gravimetric capacity

Experimentally, 97% of hydrogen stored in engineered nanospaces within activated SWNHs at room temperature (up to 1.5 wt.%) is released at 3 bar pressure.

The enhanced storage capacities due to Ca decoration of SWNHs (up to 8.4 wt.%) will be utilized to address 2010 (6 wt.%) and 2015 (9 wt. %) system targets

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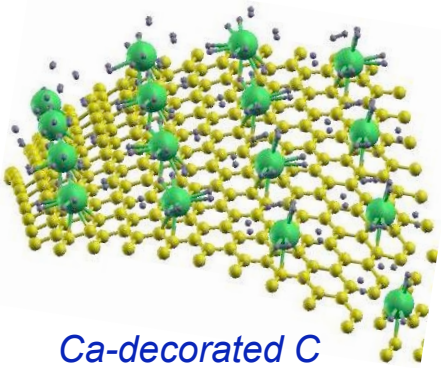
Future Work

- ***Charged Nanostructures***

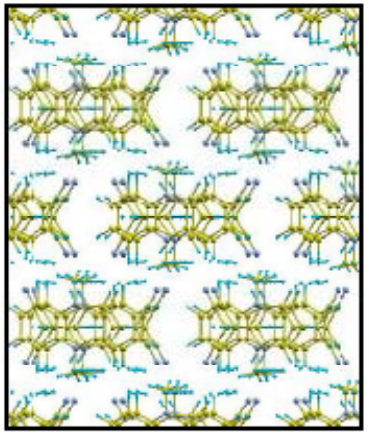
  - **Ca-SWNHs are just one example of a new class of materials emerging from this program with engineered nanopores and coatings exhibiting high permanent electric fields induced by metal decoration. Although, the preliminary hydrogen uptake results look promising (see slide #.....) more work needs to be done to optimize this material.**

  - **These concepts should be extended to commercial nanocarbons (such as activated carbons, graphene nanoplatelets, etc.) as preliminarily explored in this program.**

  - **Develop new doped, decorated, and filled charged nanostructure hybrids as outlined in this program (see next slide). We propose to explore the synthesis of these prototype structures.**



Ca-decorated C



Organic crystals

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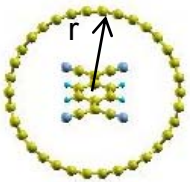
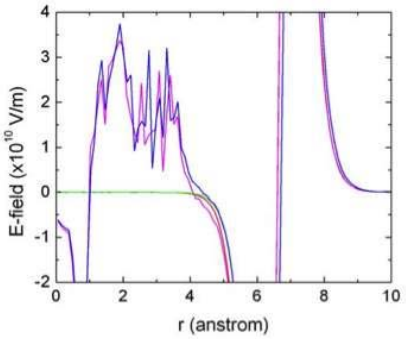
Future Work - Preliminary results

Explore the hydrogen storage properties of nanostructures with high electric fields to polarize and store H_2

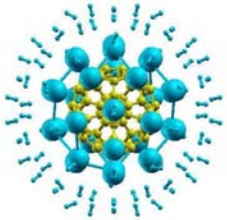
Filled





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

Coated



$92H_2$-$Ca_{32}C_{60}$ (8.4 wt%)

$\Delta E \sim 0.4 eV/H_2$

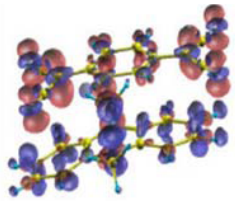
Charge transfer between supports and coatings (e.g. C and Ca in this project) can generate high E-fields for H_2 storage

Organic Crystals:

Blue: electron depletion
Red: electron accumulation

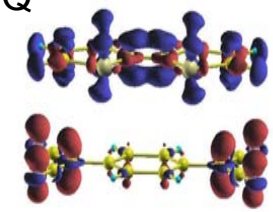
~0.5 electron transfer between DMPH and TCNQ

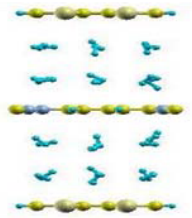
DMPH -TCNQ



8.1wt%, 65g/L H_2

TTF-TCNQ





$\Delta E \sim 0.2 eV/H_2$, ~8wt%

Organic layers and crystals self-assemble into layers with high permanent electric fields with E-fields sufficient to store H_2

The concept of 'charged nanostructures' applied to hydrogen storage being tested in this project with Ca-decorated SWNHs is a general concept which involves 1) nanoengineering space for hydrogen with 2) permanent electric fields sufficient to polarize and bind hydrogen. This can be accomplished by filling, decorating, or building nanostructures. Organic crystals appear to be very promising materials for future study.

[calculations: M. Yoon (to be submitted)]

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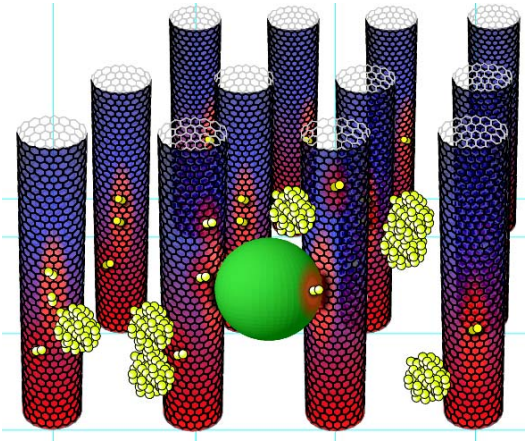
Future Work - Preliminary Results

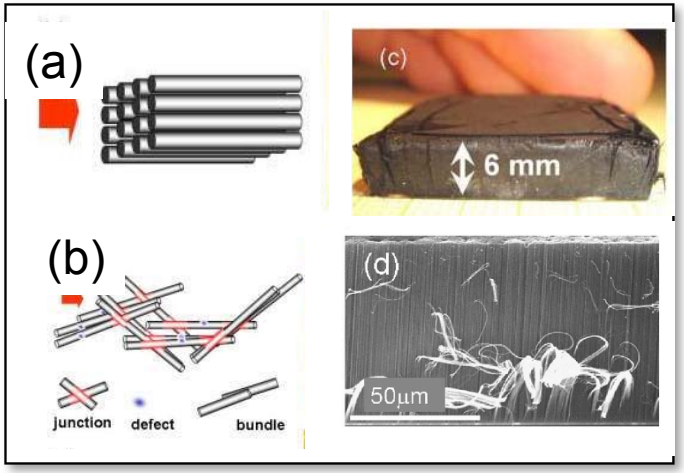
Nanohorn Composites for Faster Loading and Thermal Management

Vertically Aligned Nano-Tube Arrays - VANTAs -

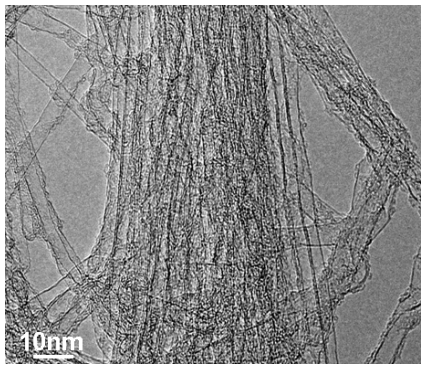
- Have been synthesized as compressible large-diameter single-walls at ORNL in multi-millimeter long bulk composites
- Have thermal conductivities which outperform any other macroscopic nanotube assembly, and are currently a factor of 3 better than currently used thermal interface materials
  - 15 ±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



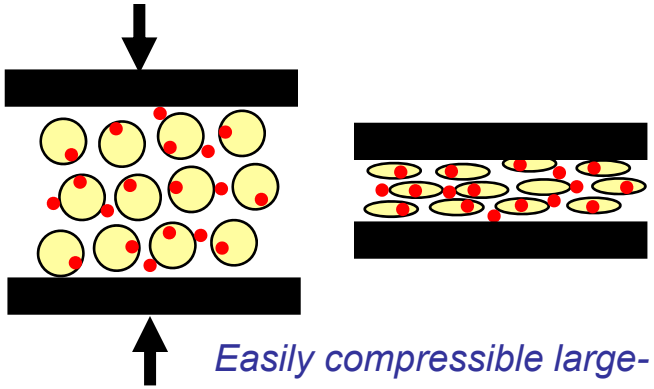
CONCEPT: Use decoration techniques and pore size optimization established for SWNHs to tailor composites with these materials to provide simultaneous storage and high thermal conductivity



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



Large diameter SWNT-VANTAs



Easily compressible large-diameter, decorated SWNT-SWNH composites

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Summary

- **Overall:** This program has demonstrated that pore sizes in carbon nanohorn aggregates can be tuned 1) during synthesis, and 2) during activation , and that this sometimes results in room-temperature binding of up to 1.5 wt.% hydrogen. The effects of metal decoration have been demonstrated. Clear spillover and enhanced binding energy were observed. Decoration with Ca has been shown to result in smooth nanoparticle-free coatings and anomalously high storage, in agreement with our proposed mechanism of *polarization induced by high local electric fields* resulting from the alkaline-earth metal "doping" of C by decoration.

- **Nanohorns: Summary of results**
  - *High surface areas*: SWNHs were synthesized in gram quantities with pore sizes adjusted to maximize surface area (2142 m^2/g) and increase excess storage (3.5 wt. % at 77K).
  - *Tunable, small pores*: NMR confirmed the majority of storage in the interstitial (~ 0.5 nm) pores on large SWNHs, and in activated pores (< 1 nm) in short-SWNHs. These NMR shifts are the highest among all materials studied, indicating storage in very small pores. Work continues to understand the activation process, but is aided by the stability of the nanohorn aggregate structure which is defined at very high temperatures during synthesis.
  - *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). These "nanoengineered pores" are defined both by the unique nanostructure self-assembled during synthesis, and by the activated pores during oxidation.
  - *Enhanced Binding Due to Metal Decoration - Doping-Induced Charge Separation -* Methods of vapor phase Ca-decoration were developed and found to result in smooth decoration unlike decoration by transition metals which results in small nanoparticles. These results confirm our theoretical predictions, which predict that of all the elements, alkaline earth metals **Ca and Sr** should have a special ability to coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H_2 with 8.4 wt. % and 0.4 eV for Ca.

- **Program Focus: Charged nanostructures for hydrogen storage**
  - Activate and Ca-decorate O-SWNHs and commercial carbons such as AX-21 for maximal H_2 uptake.
  - Theoretically search for new nanostructures with stable, dipole fields, such as organic molecule-based "ionic crystals"with sufficient internal spacing to store hydrogen.

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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 and Ca dec. "short"	O-SWNHs+Ca	212				1.9 (0.9bar)	
	O-SWNHs	1123				1.9 (0.9bar)	

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