

# Hydrogen Storage Research at Oak Ridge National Laboratory



CARBON-BASED  
HYDROGEN STORAGE  
CENTER of EXCELLENCE

## (A) Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

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## (B) Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage

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Oak Ridge, TN*

This presentation does not contain any proprietary or confidential information

Project ID STP-12

# Overall Project Overview - STP 12

## Timeline

- Project start date: FY05
- Project end date: FY09
- 20% complete

## Budget

- Total project funding
  - DOE share 3.8 M\$
  - Contractor share 0k
- 400k received in FY05
- 600k received in FY06

## 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

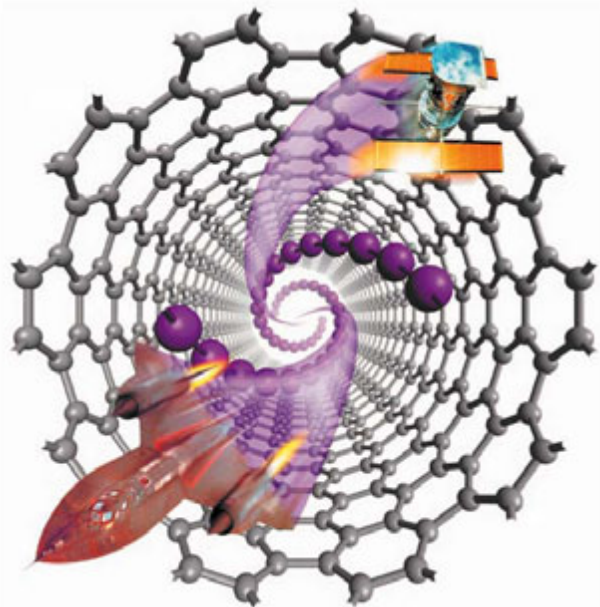
## Partners

- Participants in the MHCoe
- Participants in the CbHSCoe

# (A) Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

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Oak Ridge National Laboratory, Oak Ridge, TN  
Participants in the DOE Center of Excellence on Carbon-based Hydrogen Storage Materials  
DOE Hydrogen Program Annual Review, Washington, D.C., May 18, 2006*

# Project Overview - STP 12

## (A) Single Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

### Timeline

- Project start date: FY05
- Project end date: FY09
- 20% complete

### Budget

- Total project funding
  - DOE share 1.9 M\$
  - Contractor share 0k
- 200k received in FY05
- 300k received in FY06

### 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

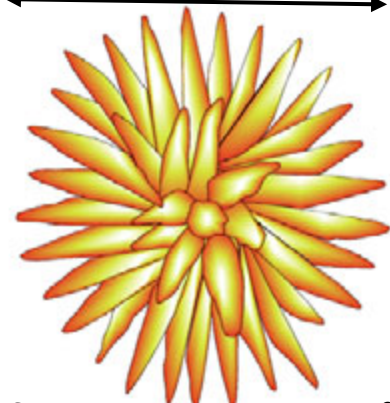
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Overall	To control the synthesis and processing of a novel form of carbon – <i>single walled carbon nanohorns</i> – as a medium with tunable porosity for optimizing hydrogen storage
2005	Develop high-power laser vaporization synthesis facility to produce SWNHs with controllable structure
2006	<ul style="list-style-type: none"><li>A) Apply <i>in situ</i> diagnostics to understand and control nanohorn formation for production of SWNHs with controllable structure in gram quantities</li><li>B) Develop chemical and thermal processing treatments to adjust and tune porosity of SWNHs, and decorate them with metal clusters</li><li>C) To work interactively with CbHS Center members to understand how to optimize these materials and their composites for maximal hydrogen storage consistent with DOE targets</li></ul>

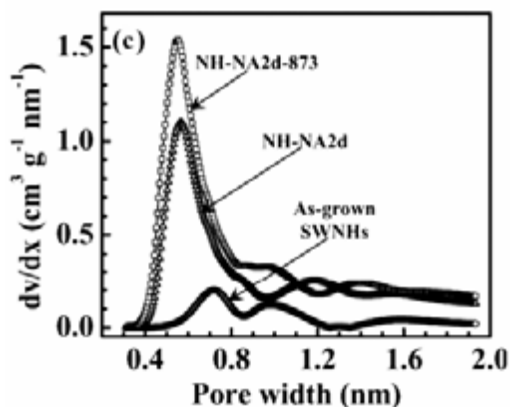
# Nanohorns - Single Wall Carbon Structures which may be Tailored as Nanoporous Materials

SWNH aggregate

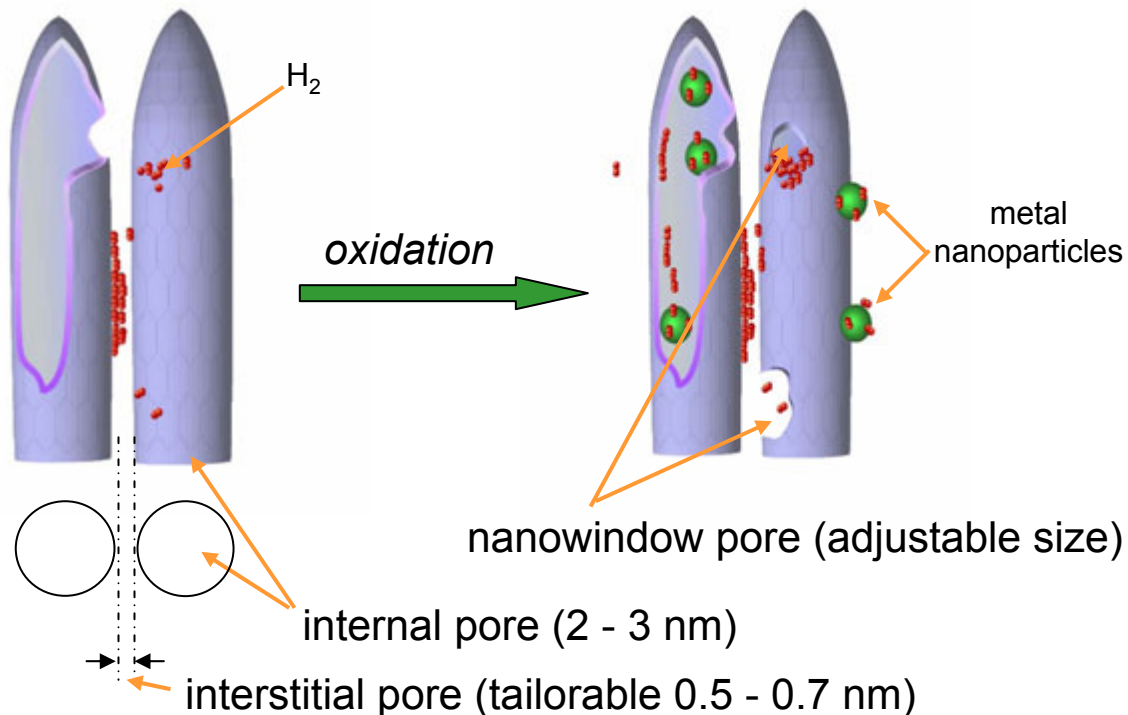
100 nm



(surface area up to 1900m<sup>2</sup>/g)



Micropore size distributions of as-grown and oxidized SWNHs determined by the HK method.



**SWNHs are single-wall carbon nanostructures synthesized free of metals. They are excellent supports for ultra-fine metal catalysts. Their pore size can be adjusted and tuned by oxidation.**

Yang et al, *Advanced Materials* 17, 869 (2005)

# Approach

## Overall

Explore SWNHs as a tailorable nanoporous single-walled carbon nanostructured medium for hydrogen storage with

- Tune nanostructure during synthesis
- Tune nanoporosity of structure during processing

## Synthesis

1. Understand nanohorn formation mechanism using in situ process diagnostics
2. Control nanohorn unit and aggregate structures
3. Produce gram quantities with controllable nanostructure

## Processing

1. Develop nanohorn chemistry to control pore size, surface area, and defects
2. Heat treatments for graphitization
3. Chemical treatments developed for metal nanoparticle decoration

## Testing

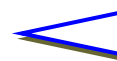
1. Relate BET, surface area measurements to nanostructure characterization (TEM, Raman, SEM, TGA)
2. Hydrogen uptake (partners)
3. NMR, neutron scattering (partners)



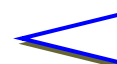
# Technical Accomplishments / Progress / Results

## Task 1: Controlled Synthesis of SWNHs - Understand Formation and Produce Gram Quantities

- In situ diagnostic studies of nanohorn formation mechanism vs. laser vaporization parameters
  - imaging and pyrometry of synthesis conditions
  - In situ DMA analysis of particle size - controllable
- Single-wall carbon nanohorns (SWNHs) with tunable morphologies can be synthesized at gram scale at ORNL for hydrogen storage.
- Modeling of laser-target heat transfer to optimize yield of nanohorns
- Safe, new collection technique developed - enabling 10 g runs
- Decoration with Ti, Pt, Pd has been accomplished in situ by LV



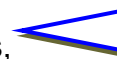
Milestone Achieved 3/06  
*Gram quantities delivered to partners*



Milestone in Progress 9/06  
*Vary synthesis parameters to produce materials with optimal H-storage*

## Task 2: Processing Chemistry - Tailor SWNH pore size, surface area, and decorate with metals

- Opened SWNHs were produced by thermal and chemical oxidation treatments.
- An assessment of methods to produce decorated SWNHs with metal nanoparticles has been accomplished.
- Different types of SWNHs, including unopened SWNHs, Pt decorated unopened SWNHs, opened SWNHs, Pt decorated opened SWNHs, have been delivered to the CbHSC collaborators (NREL, Air Products, NIST, and CalTech) for hydrogen uptake measurements.



Milestone Achieved 3/06  
*Preliminary review of thermal and oxidative treatments on nanohorn morphology and metal nanoparticle size distributions (to change graphitic structure) completed*

## Results: Hydrogen uptake, neutron scattering, NMR, BET

- The highest surface area of opened SWNHs obtained so far is 1892 m<sup>2</sup>/g
- Five different varieties of nanohorns have been produced and shipped to five different CbHSC partners for measurements
  - As-produced, (laser)metal-decorated, metal-decorated, opened, and opened/metal-decorated.
  - Opened SWNHs exhibit 2X higher H<sub>2</sub> storage than unopened
    - Room temperature results range from (0.2 - 0.4 wt.%)
    - 77K uptake (1 - 4 wt.%)

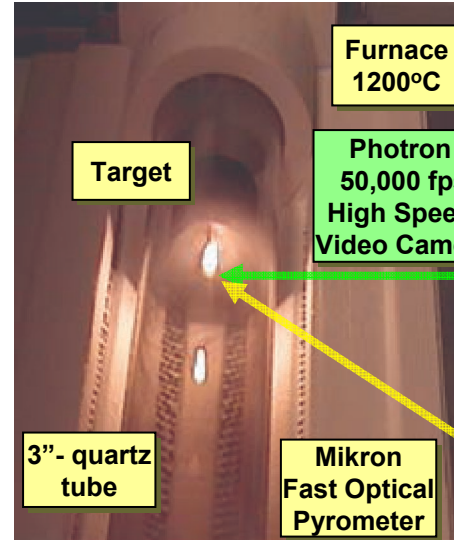
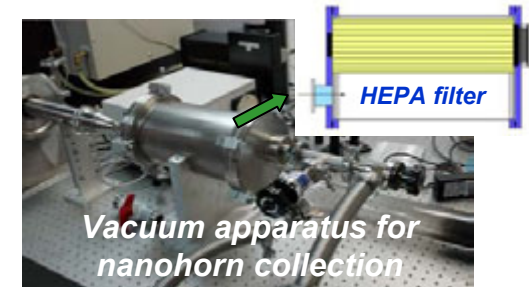
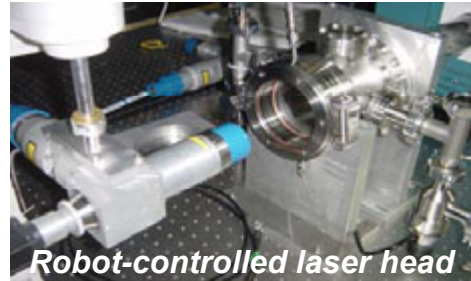


Milestone in Progress 9/06  
*Optimize chemical processing to vary pore size and graphitic structure to optimize hydrogen uptake based on partner feedback*

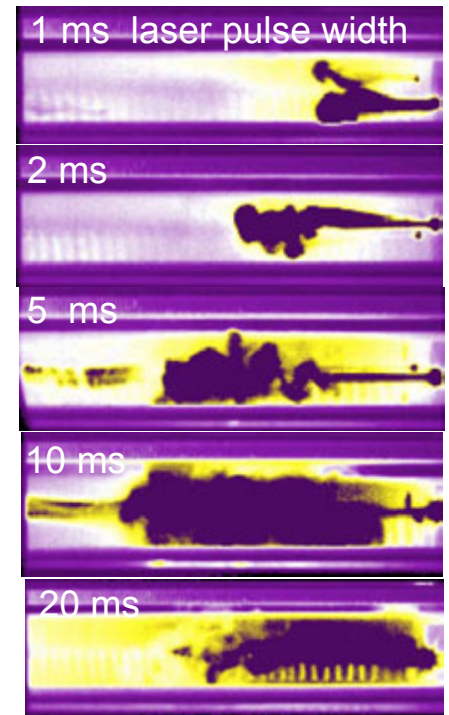


# Experimental Setup and In situ Diagnostics of SWNH Growth by Laser Vaporization

- **High power laser vaporization facility at ORNL**
  - 20 grams SWNHs / run
  - Laser safe, HEPA filtered safe collection under argon
- **Videography**
  - to understand synthesis time and confinement volume
- **Optical Pyrometry of target surface**
- **Differential Mobility Analysis measurements of particle size distributions in situ**
- **Rapid Sampling of Products**
  - For ex situ HRTEM, FESEM, TGA



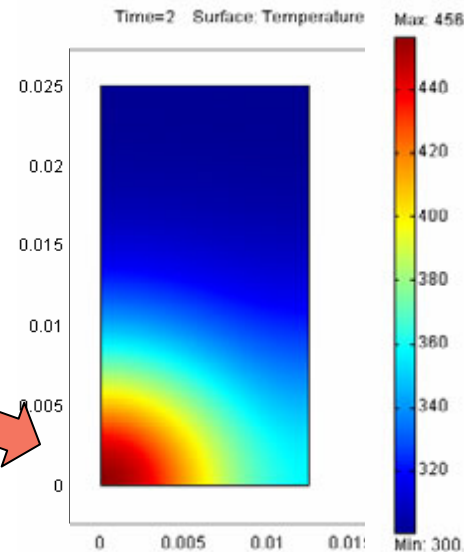
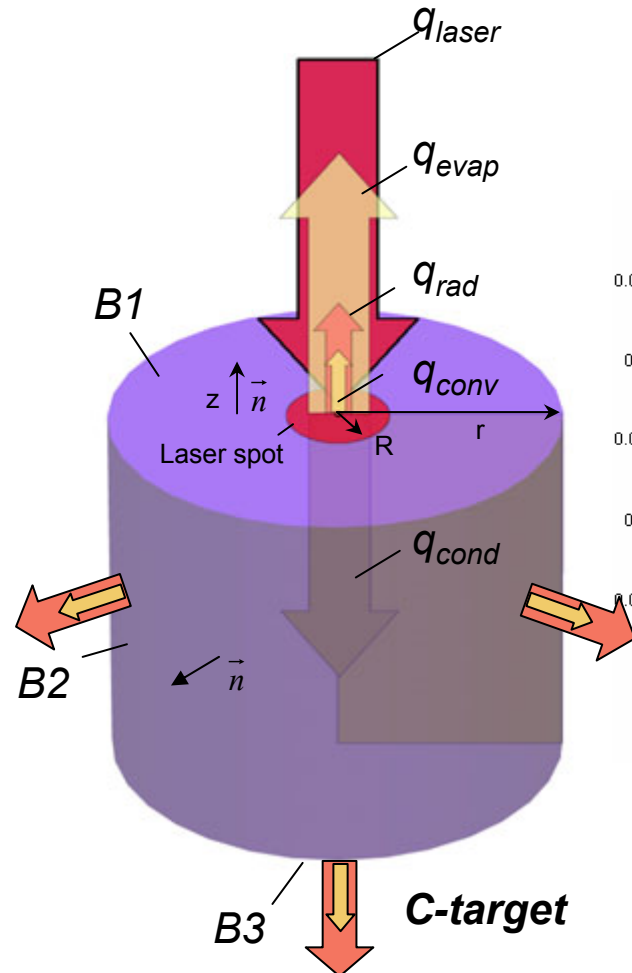
Images of laser ablation plumes



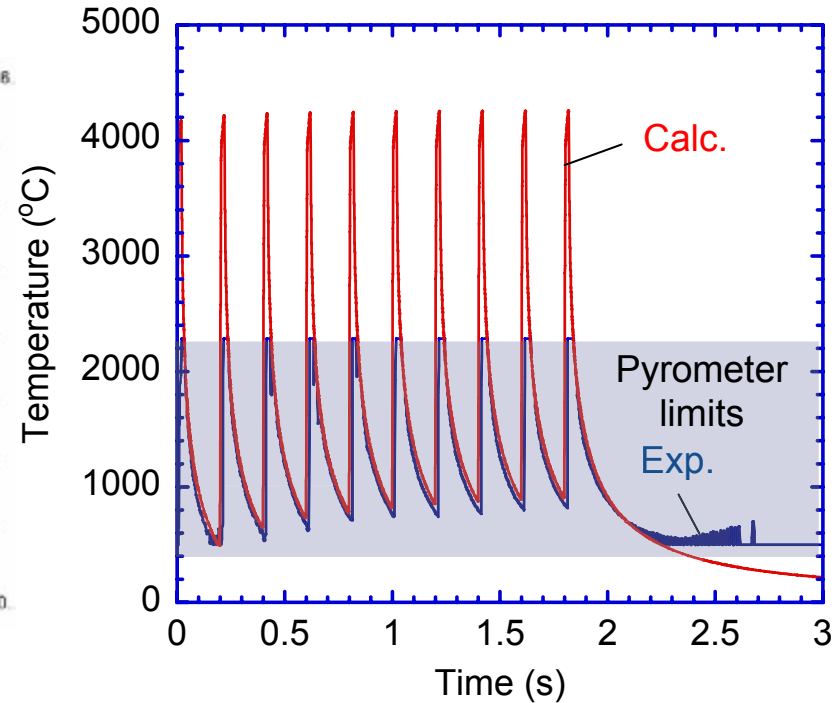
Short pulses (< 5 ms): plume cools ~ 7 ms  
Long pulses (> 10 ms): plume cools ~ 14 ms

High power laser vaporization apparatus was developed for nanohorn production at elevated temperatures and safe collection without air exposure. Three different *in situ* techniques were applied to understand and control nanohorn morphology.

# 3D-Modeling and Fast Pyrometry Measurements of Target Temperature Distribution During Pulsed Laser Irradiation

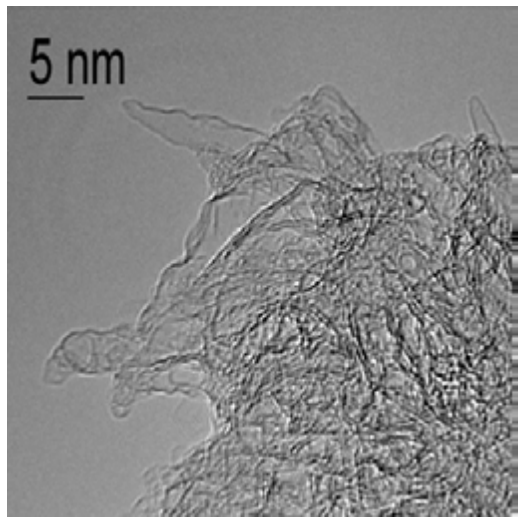


*Long pulse*  
20ms, 5Hz, 100J/pulse

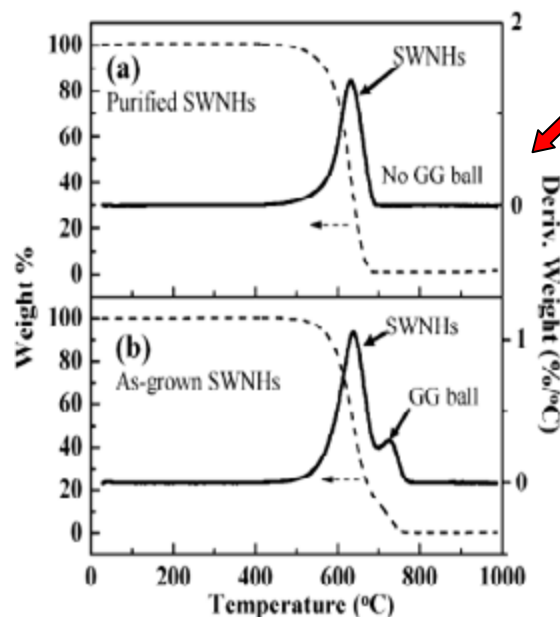
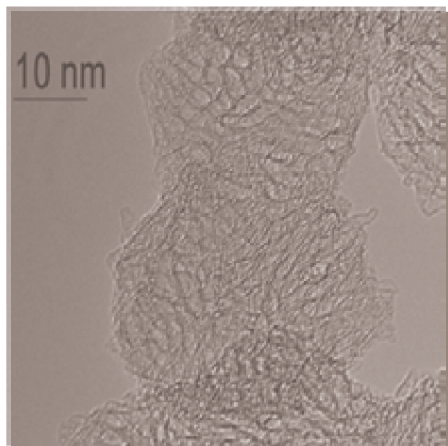


The heat transfer characteristics of the target were determined by in situ pyrometry and computer simulations to develop laser scanning patterns for consistent, high-yield SWNH production.

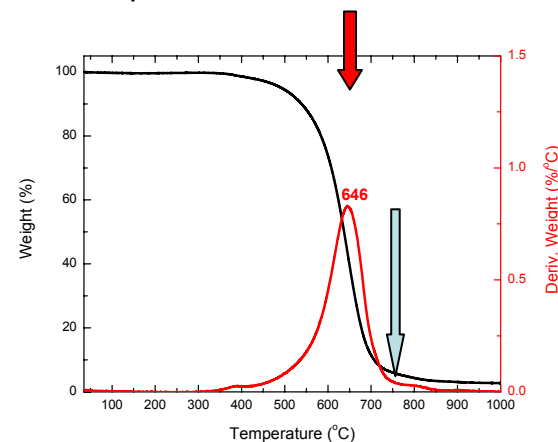
# High Purity as-prepared SWNHs (AP-SWNHs): Produced at ORNL by Laser Vaporization at Elevated Temperatures



*TEM and SEM of SWNH produced with high-power 600W ORNL Nd:YAG laser vaporization*



*SWNHs synthesized by Iijima group show graphitic particle impurities burning at ~750°C before purification [JPCB 2005], which are NOT observed in as prepared SWNHs produced at ORNL.*



**AP-SWNHs produced in this project do not contain graphitic impurities.**

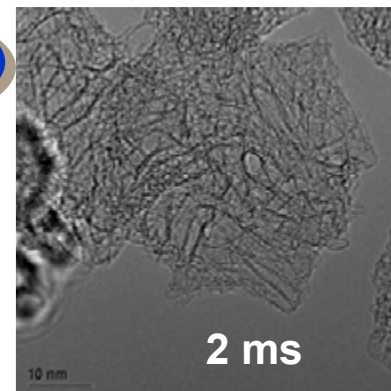
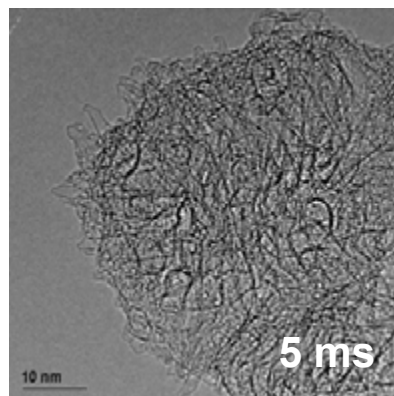
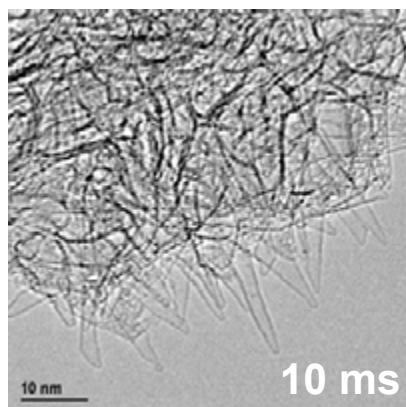
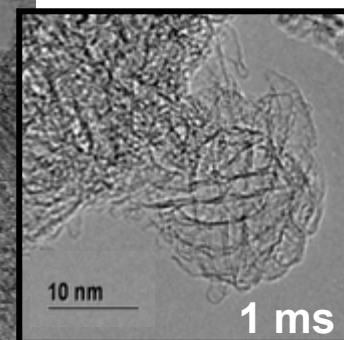
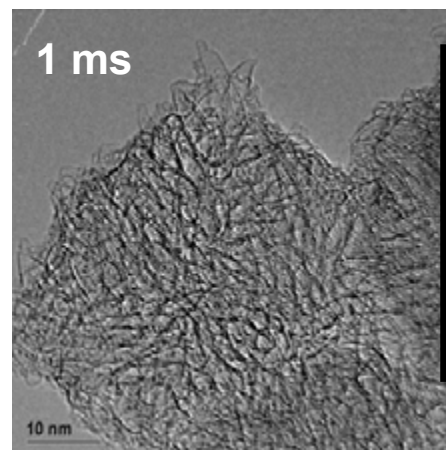
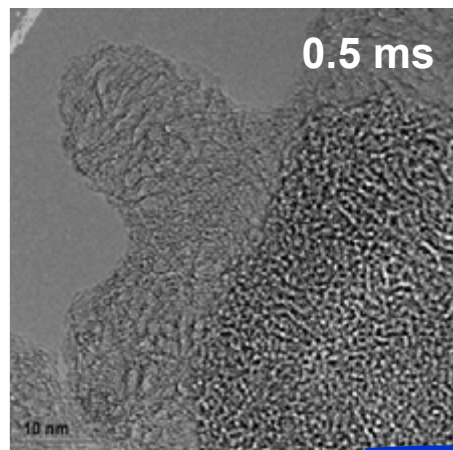
# Nanohorn Morphology vs. Laser Pulse Width

✓ *Nanohorns found at all pulse widths > 0.5 ms*

✓ *Nanohorn fraction vs. a-C increases with pulse width*

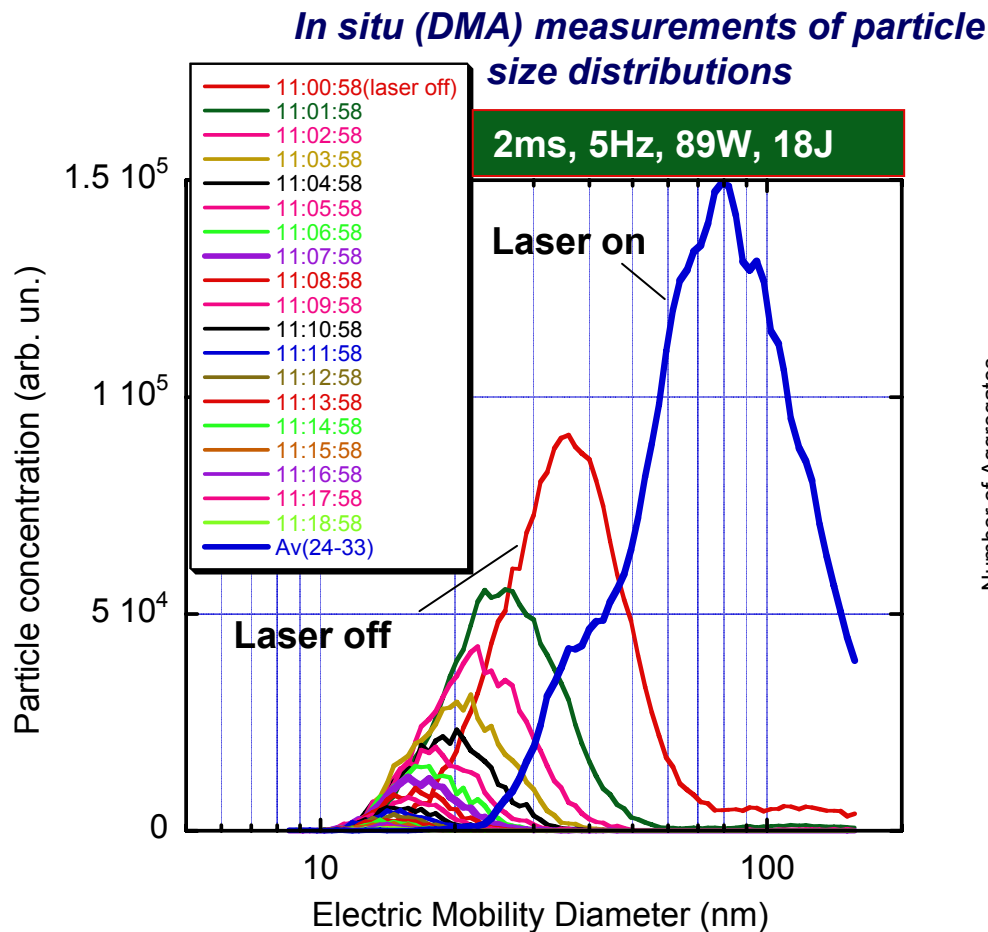
✓ *Nanohorn length increases with pulse width*

✓ *Aggregate size increases with pulse width*

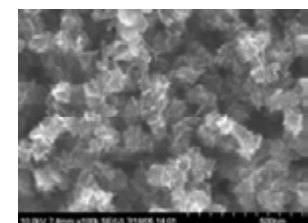
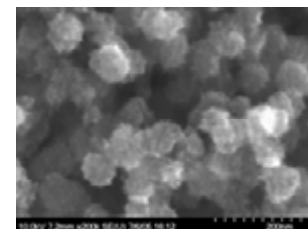
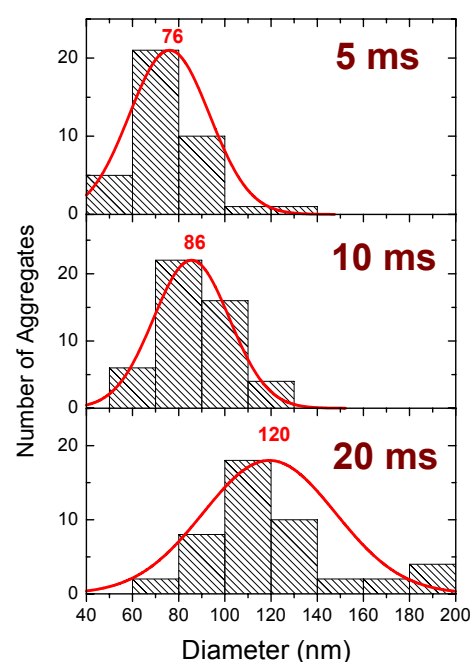


The morphology of SWNHs were varied by changing laser pulse widths.

# Nanohorn Aggregate Size vs. Laser Pulse Width



*Ex situ SEM analysis of particle size distributions at different laser pulse widths*

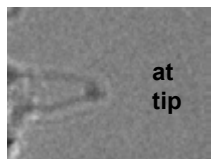
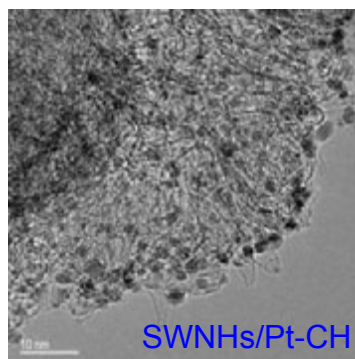
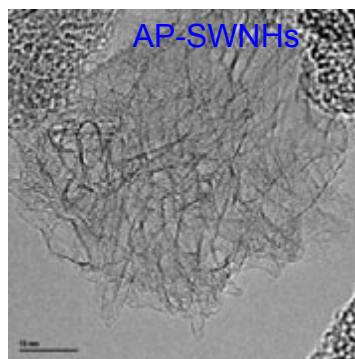
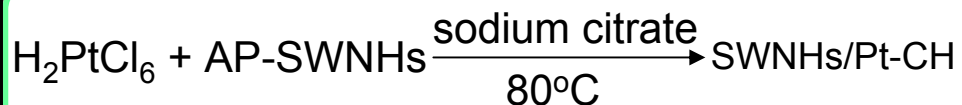


100 mg SWNHs  
compressed  
Bulk density  $\rho = 0.5 \text{ g/cm}^3$

Size distributions of SWNH aggregates can be varied by changing laser pulse widths. The effects of aggregate size on compressed bulk density are under study.

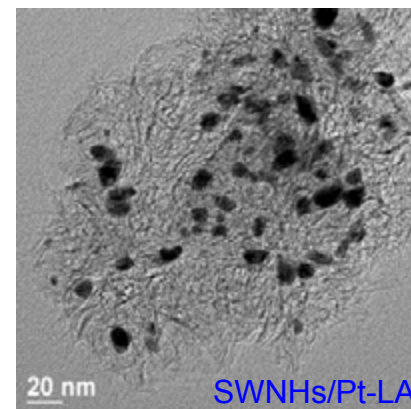
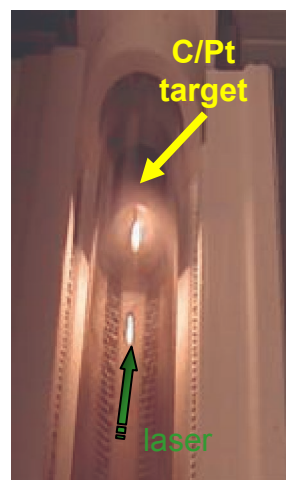
# Pt Decoration of As-Prepared SWNHs (AP-SWNHs)

## Method 1: In-situ Decoration via wet chemistry



- Homogeneous decoration (TEM)
- Small size of Pt nanoparticles (1-3 nm)
- High Pt loading: 20wt% (TGA)

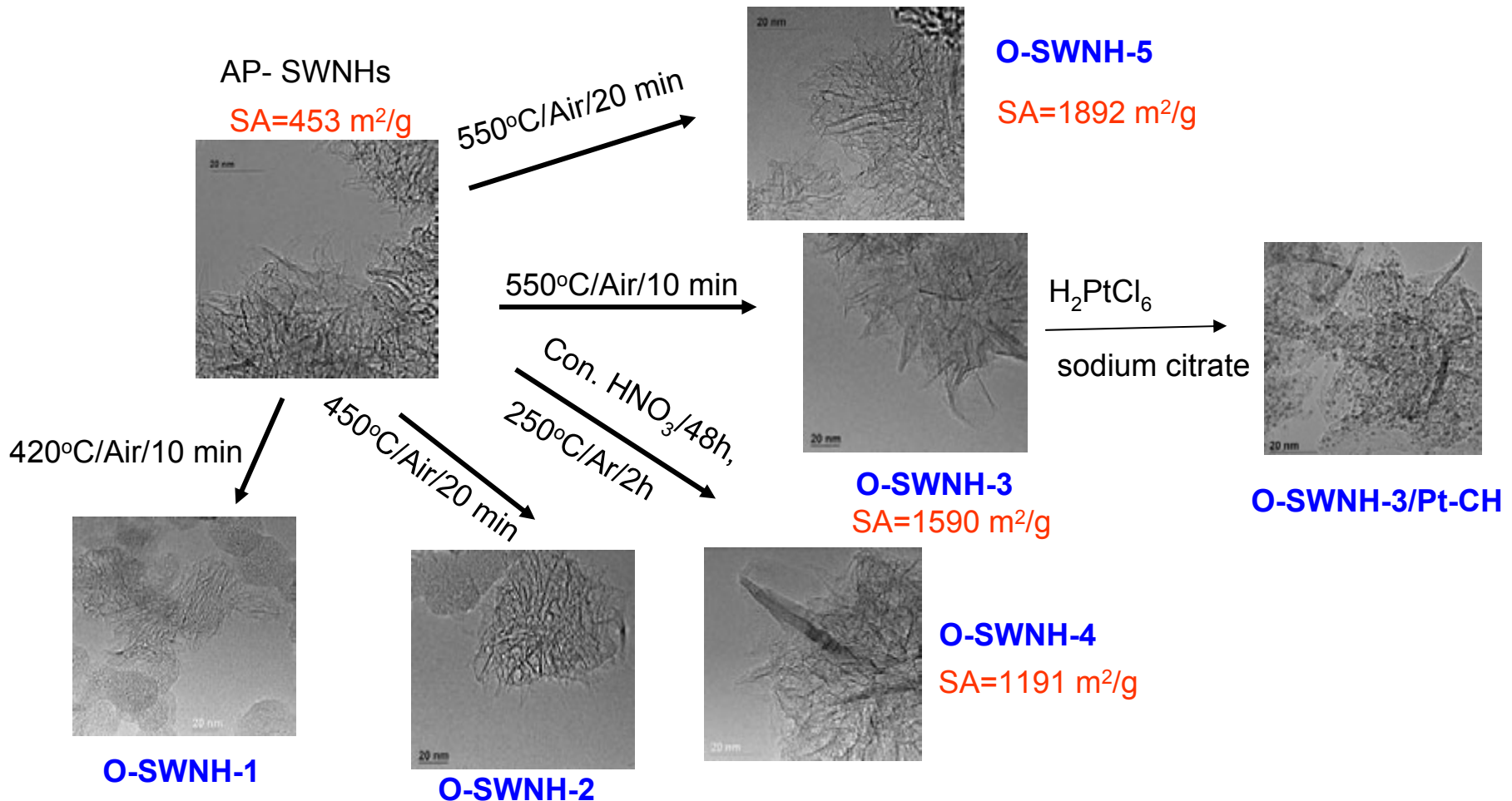
## Method 2: Laser Ablation using C/Pt Target



- Large-scale synthesis (gram scale)
  - Broad size distribution of Pt NP (1-10 nm)
  - Pt loading ~15 wt% (TGA)
- Weight Ratio: Pt/C = 13.5 % (PGAA) by *NIST*

Two methods have been developed to decorate SWNHs with metal nanoparticles.

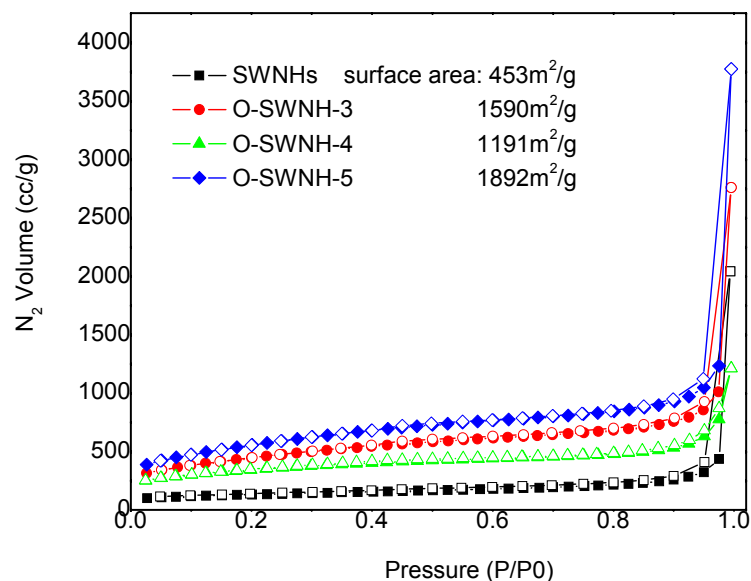
# Tailoring of SWNHs Morphology and Structure by Thermal and Chemical Oxidation Post-Treatments



Thermal and chemical oxidation treatment have been explored to adjust the surface area and pore size of SWNHs.

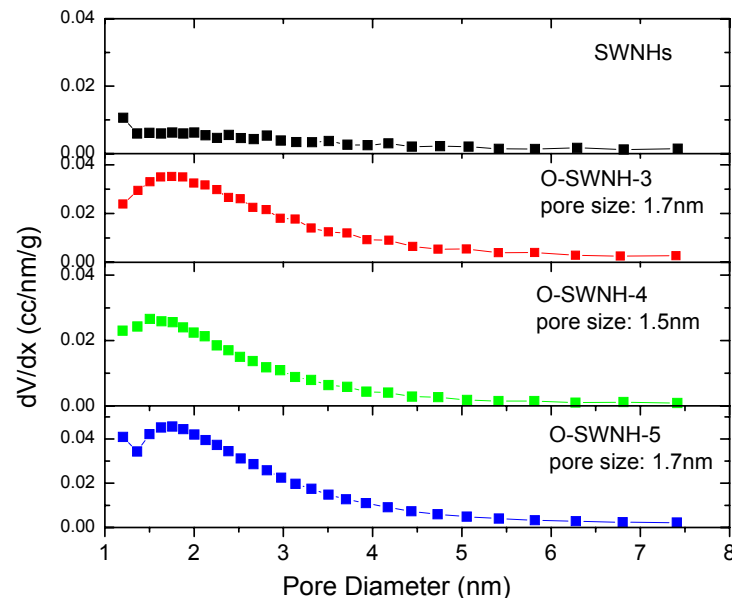
# Adjustment of Surface Area and Pore Size of SWNHs

## Isotherm adsorption



- *N<sub>2</sub> adsorption isotherms of AP-SWNHs and O-SWNHs at 77K in a linear scale of the relative pressure.*

## Pore size distribution



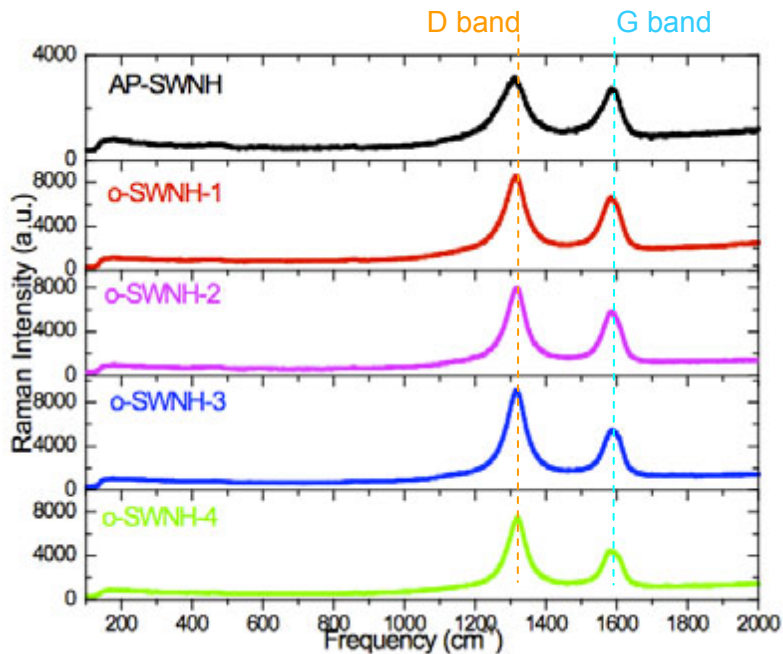
- *The mesopore size distribution of AP-SWNHs and O-SWNHs by the BJH method.*

Opened SWNHs have surface areas (1892 m<sup>2</sup>/g) up to 4 times that of unopened AP-SWNHs (453 m<sup>2</sup>/g) and adjustable pore sizes of 1.5~1.7 nm.



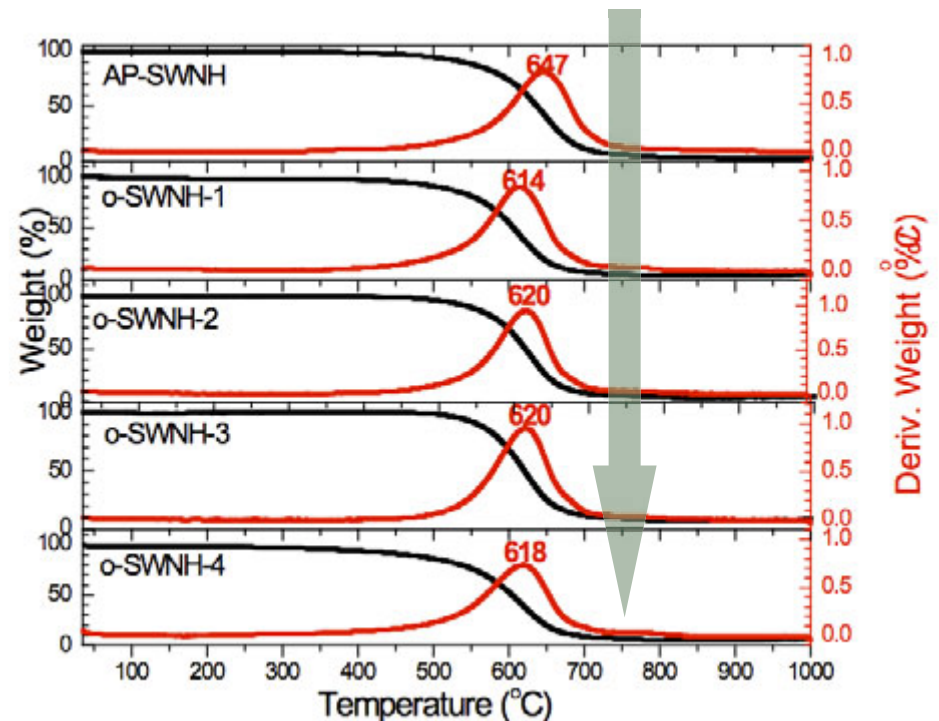
# Characterization of Opened SWNHs

## Raman spectroscopy



- *D:G ratio correlates with surface area*
- *O-SWNHs have higher D:G (1.3~1.6) than that of SWNHs (1.2)*

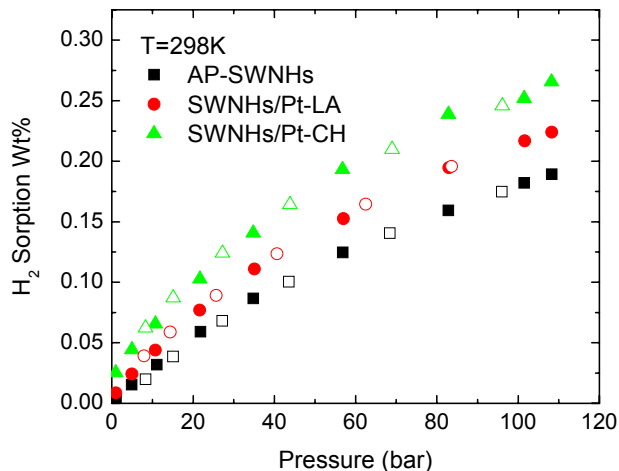
## TGA data



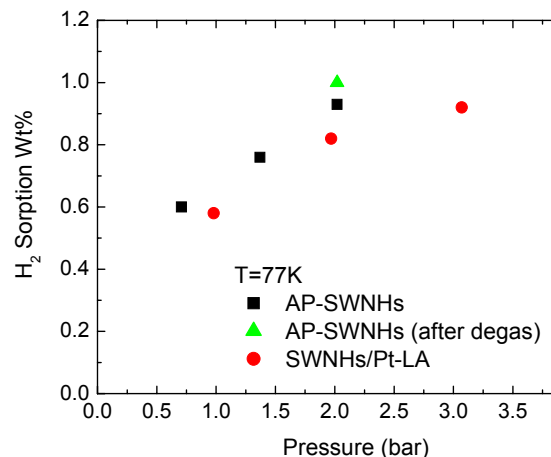
- *No graphitic particles peak (~750°C)*
- *O-SWNHs burn at lower Temp*

Raman and TGA have been used to monitor the opening of SWNHs and to judge the surface area.

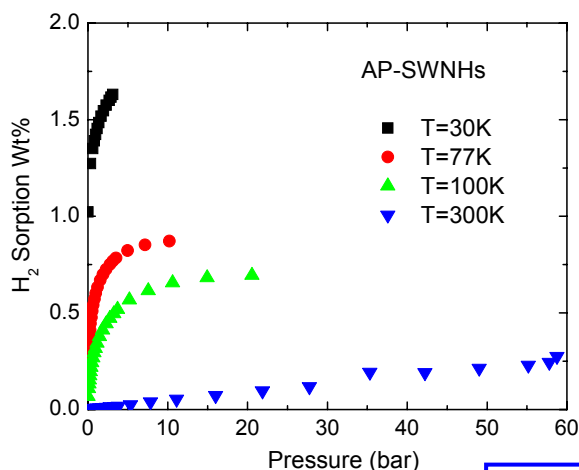
# Summary of Hydrogen Isotherm Measurements on AP-SWNHs and SWNHs/Pt by Our Partners



**API, 298K**  
 up to 110 bar  
0.2~0.3 wt%

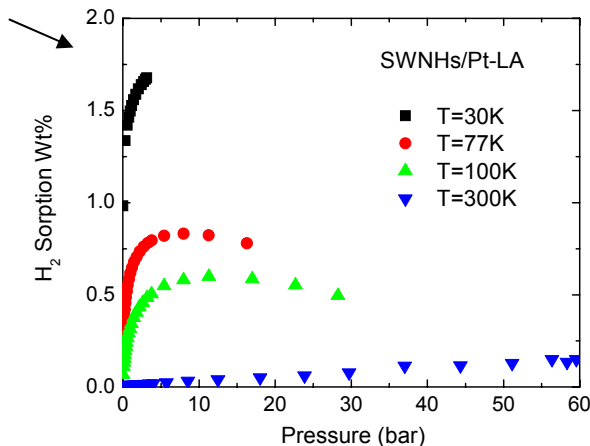


**NREL, 77K**  
 up to 3 bar  
~1.0 wt%



**NIST, varied T**  
 up to 60 bar

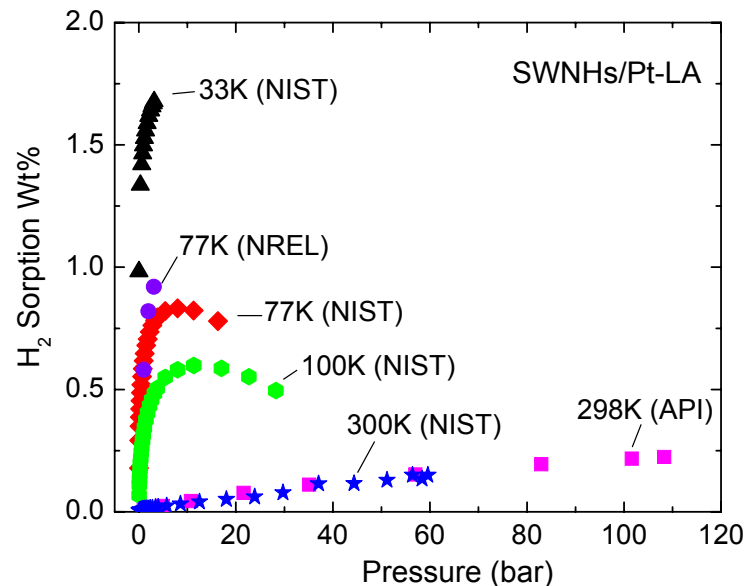
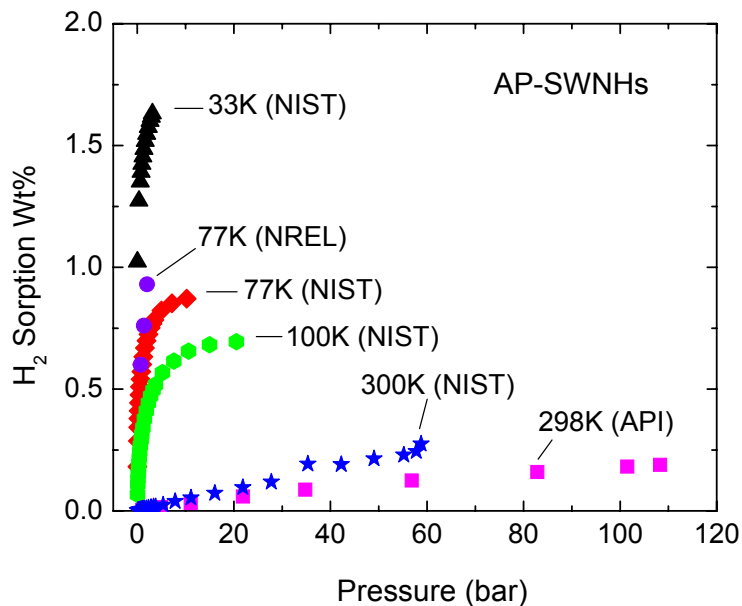
~1.7 wt% at 30K  
~0.8 wt% at 77K  
~0.6 wt% at 100K  
~0.2 wt% at 300K



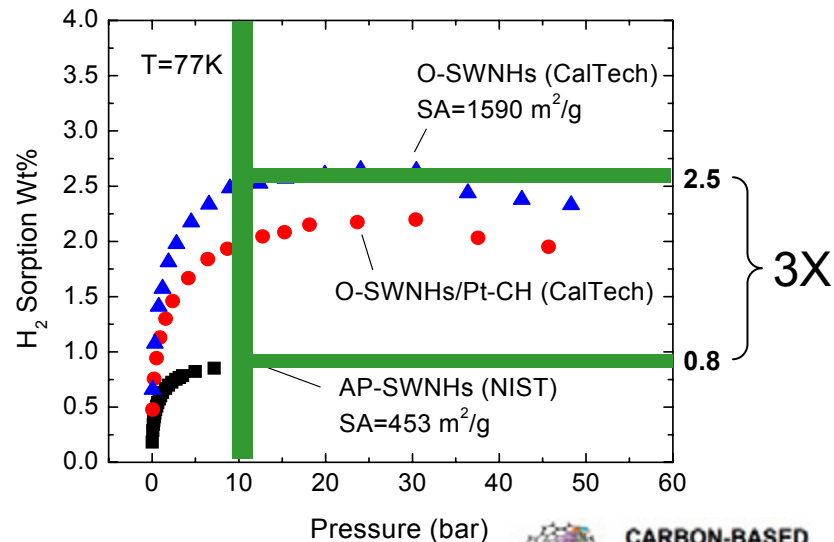
**Hydrogen uptake capability of different types of SWNHs have been assessed by our partners.**



# Hydrogen Isotherm Comparisons on AP-SWNHs, SWNHs/Pt and O-SWNHs

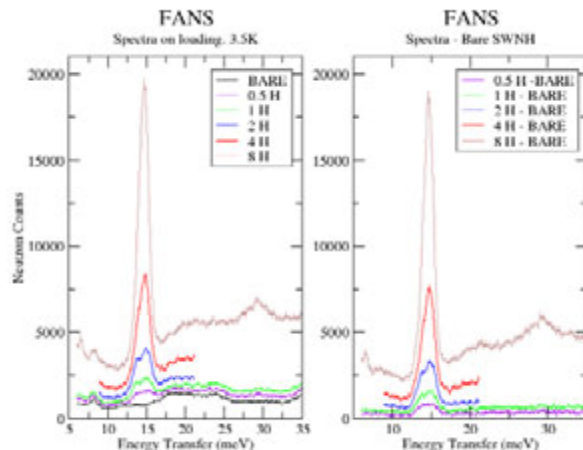


**Opened SWNHs have 3X uptake of unopened AP-SWNHs and SWNHs/Pt, which exhibit similar hydrogen uptakes.**



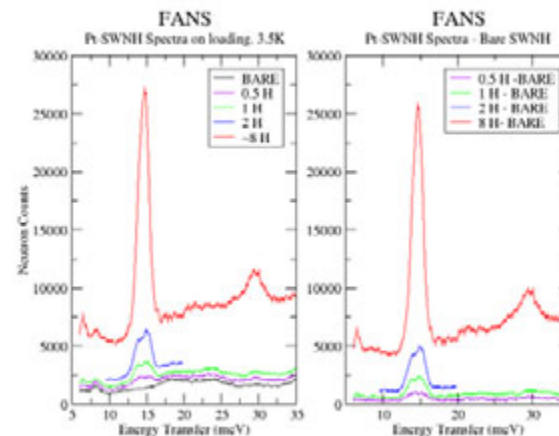
# Neutron Vibrational Spectroscopy – measured by *NIST*

**SWNH**



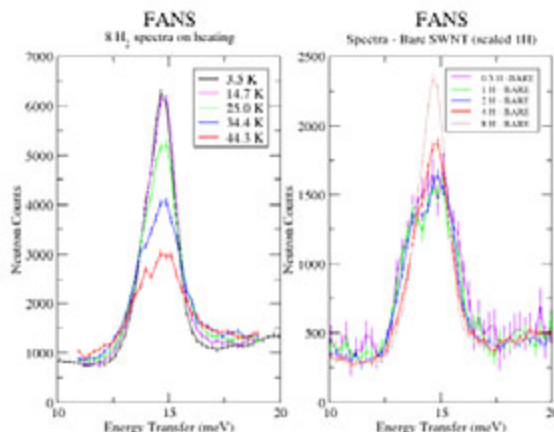
Left: Raw data with H<sub>2</sub> loading.  
Right: With bare material subtracted.

**SWNH/Pt**



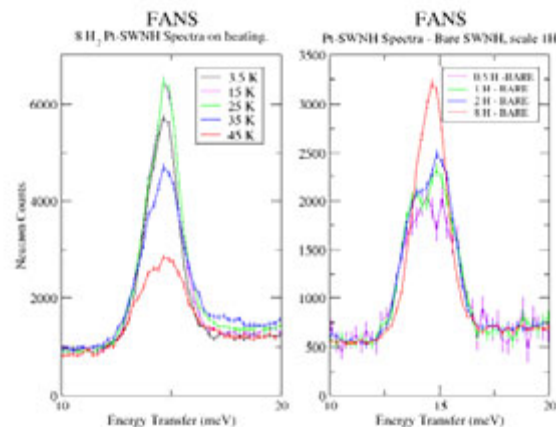
Left: Raw data with H<sub>2</sub> loading.  
Right: With bare material subtracted.

**SWNH**



Left: Fully loaded H<sub>2</sub> data on heating.  
Right: 3.5 K data scaled to 1 H<sub>2</sub>

**SWNH/Pt**



Left: Fully loaded H<sub>2</sub> data on heating.  
Right: 3.5 K data scaled to 1 H<sub>2</sub>

**AP-SWNHs and SWNHs/Pt  
exhibit similar uptake kinetics.**



# Summary

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- **Single-walled carbon nanohorns are a unique form of nanoporous carbon with the capability of being produced in high volumes with tunable porosity to optimize hydrogen storage. We have demonstrated two methods for adjustment of these materials:**
  - **Synthesis**: Nanohorn synthesis and morphology has been varied, understood, and controlled through *in situ* diagnostic measurements to produce high-purity SWNHs in gram quantities with different pore sizes and structures for supply to our CbHSC partners
  - **Processing**: Chemical and thermal processing treatments have been developed to adjust and tune the porosity of SWNHs, and decorate them with very fine metal clusters in high loadings to alter their hydrogen storage capabilities.
  - The optimal nanohorn morphology and processing treatments for maximal hydrogen adsorption are under investigation.
- **Hydrogen uptake, NMR, BET, and neutron scattering measurements have been performed by CbHSCoE partners for 4 different classes of SWNHs. Benchmarks are listed below.**



# Summary Table

	Production Rate (g/hr)	SWNHs Types Produced		Surface Area (m <sup>2</sup> /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	1191, 1590, 1892	1.5, 1.7		2.5 (SA 1590)	
		opened and Pt decorated	O-SWNHs / Pt-CH				2.2	13
System Target						6 in 2010	45 in 2010	



# Future Work

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## FY'06

- **Synthesis**

- Gram quantities of SWNHs synthesized and delivered to participants. In situ metal decoration demonstrated. *Milestone 3/06 completed.*
- Determine how synthesis conditions can be adjusted to tune SWNH porosity, surface area, and graphitic structure for higher hydrogen uptake while maintaining purity. *Milestone 9/06 (work in progress)*
- *In situ* Metal Decoration - Develop process understanding to control metal cluster size.

- **Processing**

- Preliminary review and demonstration of thermal and oxidative treatments to vary nanohorn morphology and graphitic structure, and methods developed for metal nanoparticle decoration through chemical processing *Milestone 3/06 completed*
- Post-processing treatments developed (chemical decoration, heat, acid etching, oxidation) to vary pore size and metal cluster loading. Preliminary assessment of optimal parameters (SWNH pore sizes and surface areas, metal catalyst types, loading ranges, size distributions,) yielding increased hydrogen uptake. *Milestone 9/06 (work in progress).*
- Assess Pd, Ti, Ni decorated SWNHs- expect 4X increase for SWNHs/Pd vs. AP-SWNHs.

# Future Work

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## FY'07

- **Further develop SWNH synthesis and chemical processing techniques to nano-engineer SWNHs and SWNH-composites with tunable pore sizes to maximize hydrogen storage and evaluate:**
  - **Supercritical hydrogen adsorption at 77K and higher temperatures**
    - Utilize isotherm analysis to determine pores occupied at different volumetric densities.
    - Utilize neutron scattering to quantify the relative amount of hydrogen in cluster form
    - Tune SWNH/ VANTAs (Vertically-Aligned Nanotube Arrays) porosities to optimize the supercritical adsorption
    - Compare supercritical adsorption in SWNHs and VANTAs
  - **Hydrogen storage on supported metal catalysts vs. metal-catalyzed “spillover” onto graphitic nanocarbons**
    - Produce metal catalyst decorated SWNHs for use as spillover catalysts
    - Compare with direct adsorption on metal decorated SWNHs
      - Assess effects of variable graphitic structure
    - Utilize catalyst-decorated VANTAs as spillover candidates
  - **Synthesize doped SWNHs**
    - Boron, boron/magnesium, ...
    - Assess effects on hydrogen uptake
    - Explore as mechanism to alter SWNH synthesis and tune SWNH structure
    - Compare with hydrogen storage on doped SWNTs



# Critical Assumptions and Issues

- **Supercritical adsorption mechanism**  
Certain SWNH pores store H<sub>2</sub> at 70g/L at 77K. How? The mechanism needs to be clarified. Methods to optimize adsorption in all pores at this level, and at higher temperatures, must be developed.
- **Tunable Porosity and Structure**  
Continue understanding of how to adjust the pore size, surface area, and graphitic structure of opened carbon nanohorns by thermal treatment and chemical oxidation for optimal hydrogen uptake and volumetric targets.
- **Scaled Synthesis and Cost Effective Metal Decoration**  
Continue development of scaled-up synthesis of opened carbon nanohorns and *in situ* decoration of carbon nanohorns with even finer precious metals (Pt, Pd) which maintain their size with repeated cycling.
- **Effect of Metal Decoration - Spillover vs. Storage**  
Assessment of the effects of metal decoration on hydrogen uptake using opened carbon nanohorns
  - O-SWNHs/Pd expected 4X uptake than O-SWNHs
  - > 10 wt.% possible @ 77K
- **Multifunctional Composites with High Thermal Conductivity**  
Utilize pore sizes determined for optimal SWNH storage to design arrays of vertically-aligned nanotubes with similar diameters and pore sizes to provide a strong composite with high thermal conductivity and high thermal conductivity.

P. Lack of Mechanism Understanding

A. Weight and Volume

B. Cost

D. Durability / Operability

P. Lack of Mechanism Understanding

C. Efficiency / Thermal Management

# Publications and Presentations

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- ***“Decoration of single-wall carbon nanohorns with Metal nanoparticles for Hydrogen Storage”***, H. Hu, B. Zhao, A. A. Puzetky, D. Styers-Barnett, C. M. Rouleau, H. Cui and D. B. Geohegan, Materials Research Society Spring Meeting, San Fransisco, CA, April 17-22, 2006.
- ***“Synthesis of Single Wall Carbon Nanotubes and Carbon Nanohorns by High Power Laser Vaporization”***, D. B. Geohegan, A. A. Puzetky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, I. N. Ivanov, P. F. Britt, APS March Meeting 2006, Baltimore, MD, March 13-17, 2006.
- ***“Synthesis of Single Wall Carbon Nanotubes and Carbon Nanohorns by High Power Laser Vaporization”***, A. A. Puzetky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, Z. Liu, I. N. Ivanov, P. F. Britt, and D. B. Geohegan, Photonics West, SPIE, Conference 6106B, Synthesis and Photonics of Nanoscale Materials, San Jose, California, January 21-26, 2006.
- ***“In situ Investigations of Single Wall Carbon Nanohorn Synthesis by High Power Laser Vaporization”*** D. B. Geohegan, A. A. Puzetky, D. Styers-Barnett, H. Hu, C. M. Rouleau, H. Cui, Z. Liu and B. Zhao, Materials Research Society Fall Meeting 2005 Symp. A10, Boston, MA, Dec 2, 2005.
- ***“Decoration of single-wall carbon nanohorns with Pt Nanoparticles”***, H. Hu, B. Zhao, A. A. Puzetky, D. Styers-Barnett, C. M. Rouleau, H. Cui and D. B. Geohegan, Materials Research Society Fall Meeting 2005 Symp. A10, Boston, MA, Dec 2, 2005.
- ***“Time-Resolved Measurements of Nanotube and Nanohorn Growth”***, D. B. Geohegan, A. A. Puzetky, D. Styers-Barnett, C. M. Rouleau, B. Zhao, H. Hu, H. Cui, I. N. Ivanov, P. F. Britt, SESAPS Annual Meeting 2006, Williamsburg, VA, November 2005.
- ***“Synthesis of Functional Single Wall Carbon Nanohorns and Nanotubes by High Power Laser Vaporization”***, D. B. Geohegan, A. A. Puzetky, H. Cui, H. Hu, C. M. Rouleau, Z. Liu, D. Styers-Barnett, I. N. Ivanov, and B. Zhao, The 8<sup>th</sup> International Conference on Laser Ablation, Banff, Canada, September 11-16, 2005.



# **(B) Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage**

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**Oak Ridge National Laboratory  
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***May 16-19, 2006***

## Project Overview- STP 12

# (B) Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage

### Timeline

- Start: March 1, 2005
- End: Sept 30, 2009
- Percent complete: 21%

### Budget

- Total project funding
  - \$1960K (DOE 100%)
- Funding received in FY05 - \$200K
- Funding for FY06 - \$300K

### Barriers

**Demonstrate by 2010 an on-board hydrogen storage system achieving 6 wt % hydrogen**

- Weight and volume
- Hydrogen capacity and reversibility
- Lack of understanding of hydrogen chemisorption and physisorption

### Partners

- Participant in the MHCoe

# Objectives

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**ORNL is developing solution-based synthetic methods for preparation of complex anionic materials and amides of light elements for reversible storage of hydrogen**

***Collaborate with MHCoe partners to demonstrate a system for the safe and cost-effective storage and delivery of gaseous hydrogen under practical operating conditions that will achieve the DOE/FreedomCAR performance targets for 2010.***

**Two General Tasks:**

**Development of synthetic methods in support of MHCoe collaborators**

**Discovery of new complex metal hydrides and amides**

# Approach

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**ORNL is developing solution-based synthesis of new and known materials using methods appropriate for scale-up to production and practical application (100g to 1kg) – conduct reactions in organic solvents and liquid ammonia**

**Two types of target materials for hydrogen storage:**

Complex Anionic Materials, MHCoE Project B

Amide/Imide (M-N-H) Systems, MHCoE Project C

**Both types of materials: (a) methods to scale-up synthesis of materials identified by MHCoE partners (b) develop new materials**

## Approach (cont'd)

**Research at ORNL takes advantage of expertise in synthesis (inorganic, organometallic and organic)**

**Synthetic Capabilities:** Synthetic methods in solution – vacuum line, Schlenk line, cannula, and glovebox methods to handle oxygen and water sensitive materials, reactions in liquid ammonia.

**Characterization Methods:** Temperature programmed decomposition, reaction products determined with mass spectroscopy, in-situ X-ray diffraction, IR and Raman spectroscopy, NMR spectroscopy, Sievert's apparatus for P-T-C determination



# Overall Technical Accomplishments/ Progress/Results

Focus of work in FY05 and first quarter FY 06 was  $\text{LiAlH}_4$  and sodium-magnesium amide systems

Investigated effect of additives on the decomposition of  $\text{LiAlH}_4$

Preparation of organometallic compounds of Ti for use as catalysts for liberation and uptake of hydrogen from  $\text{LiAlH}_4$ .

Transition to focused projects within MHCoe in second quarter of FY06. ORNL participating in:

Project B – Complex Anionic Materials (borohydrides and alanates)

Project C – Amides/Imides (M-N-H systems)



## Accomplishments/Progress/Results (cont'd)

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### Why is release of hydrogen from $\text{LiAlH}_4$ irreversible?

Study the release and uptake of hydrogen from lithium alanate with the incorporation of a Ti catalyst as an organometallic complexes of the form  $\text{TiR}_{(4-n)}(\text{AlH}_4)_n$  where R = alkyl or aryl that is thermally labile

Study the influence of additives on the release of hydrogen from  $\text{LiAlH}_4$  - influence of  $\text{BH}_4^-$  - samples prepared by ball milling

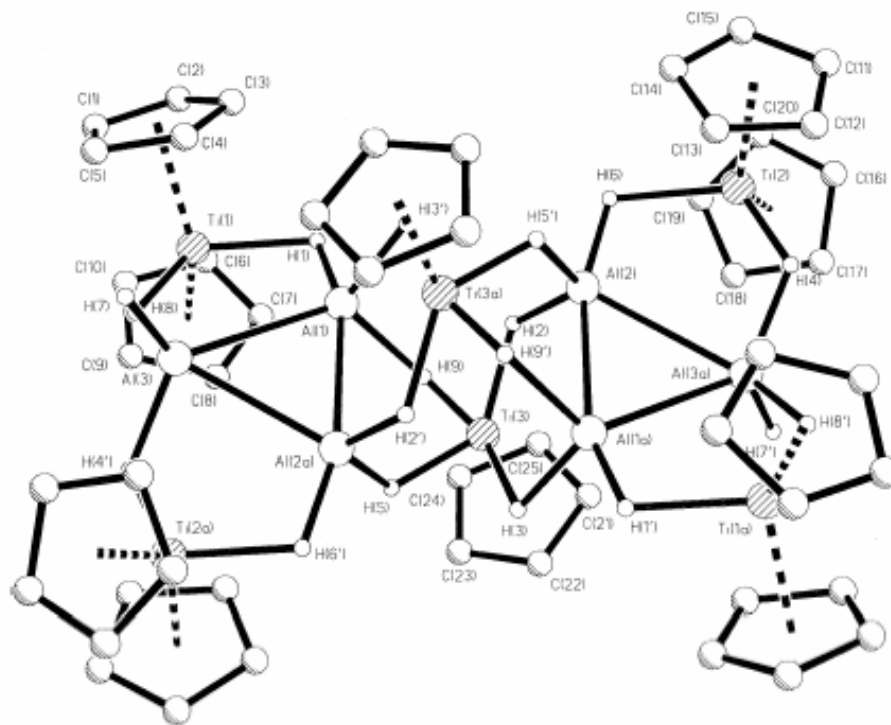
# Preparation of titanium-alanate cluster

Measure thermal hydrogen and hydrocarbon evolution – determine effect of complex on catalysis of hydrogen release and uptake from  $\text{LiAlH}_4$

Reaction of  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{AlH}_4)$  in a hydrocarbon solvent initially gives a “dimer” with bridging  $\text{AlH}_4^-$  groups and later a polynuclear complex with 6 Al atoms and 6 Ti atoms

Thermal reactions have not been systematically studied

Further reaction to evolve molecular hydrogen and hydrocarbons expected to give a very active Ti-Al catalyst



Molecular structure of the complex  $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})]_2[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\mu\text{-H}_2)\text{Al}_3(\text{m-H}_4)(\text{H})]\}$

*J. Organometal. Chem.*, **2000**, 603, 167-173.

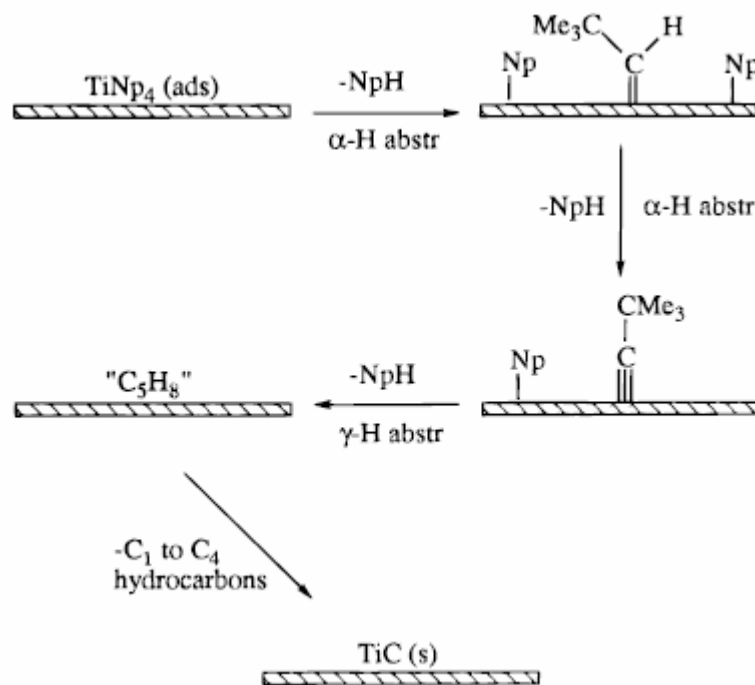
# Prepare active catalyst for hydrogen release and uptake from titanium tetraalkyl complex

Ti(neopentyl)<sub>4</sub> is an effective reagent for the deposition of TiC at low temperatures (150 °C)

Neopentyl (Np) = -CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>

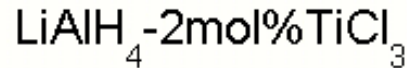
Initial decomposition product has composition "TiC" but is not crystalline ceramic material

Adsorb on solid LiAlH<sub>4</sub> from solution or allow vapor of Ti(Np)<sub>4</sub> to react with solid



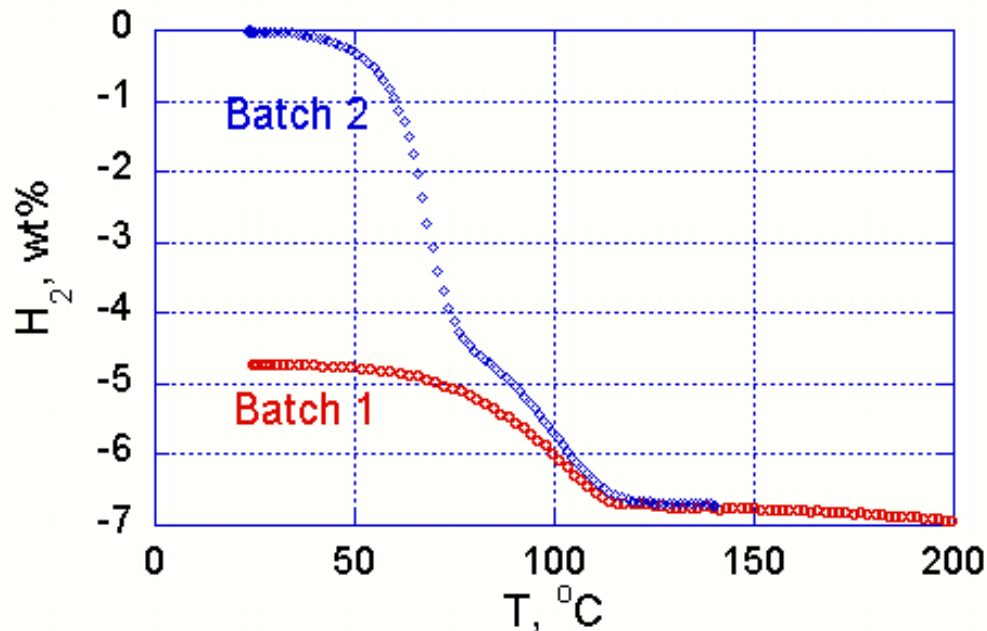
*J. Am. Chem. Soc.* **1997**, *119*, 6814-6820

# Impurities generally increase temperature for conversion of $\text{LiAlH}_4$ to $\text{Li}_3\text{AlH}_6$



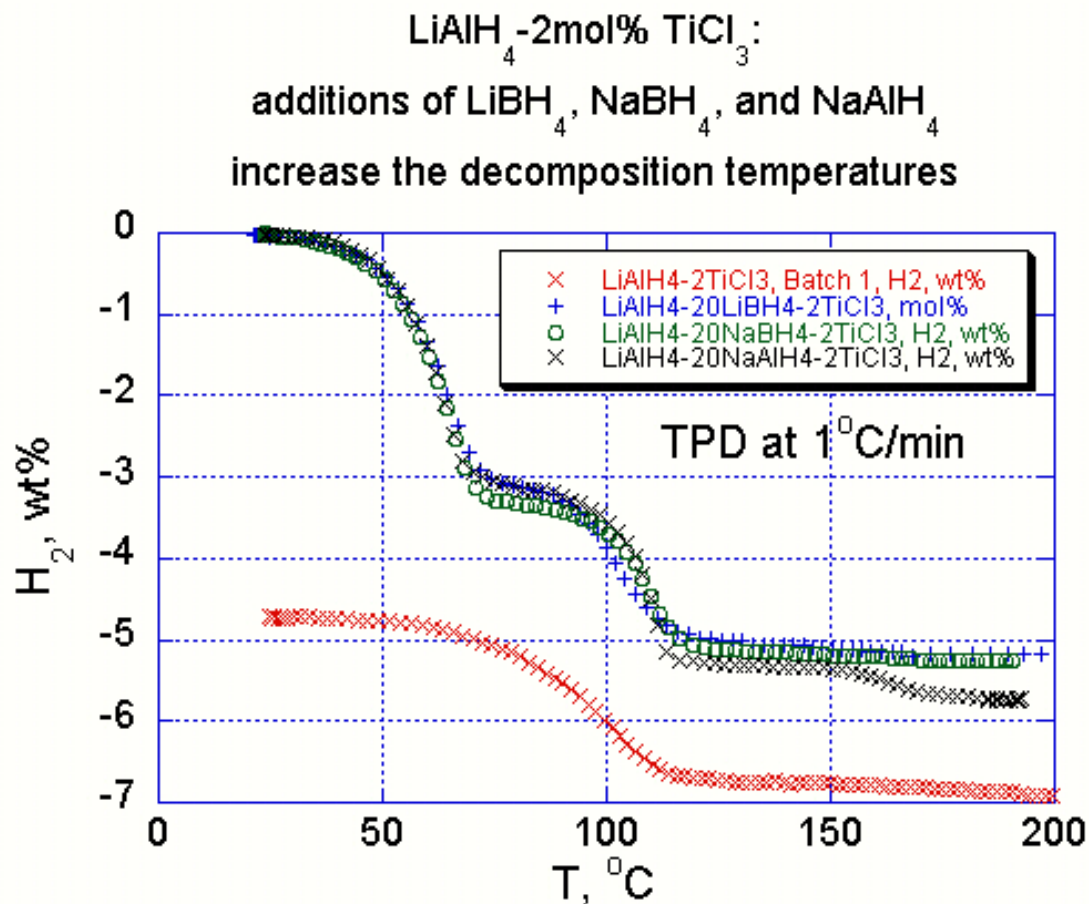
Two batches from same supplier  
Mechanically milled 30 mins

Temperature-programmed desorption at  $1^\circ\text{C}/\text{min}$



High energy milling in the presence of  $\text{TiCl}_3$  decreases temperature of conversion of  $\text{LiAlH}_4$  to  $\text{Li}_3\text{AlH}_6$  so that it occurs at room temperature for very pure material

# Influence of borohydride salts on the release of hydrogen from $\text{LiAlH}_4$

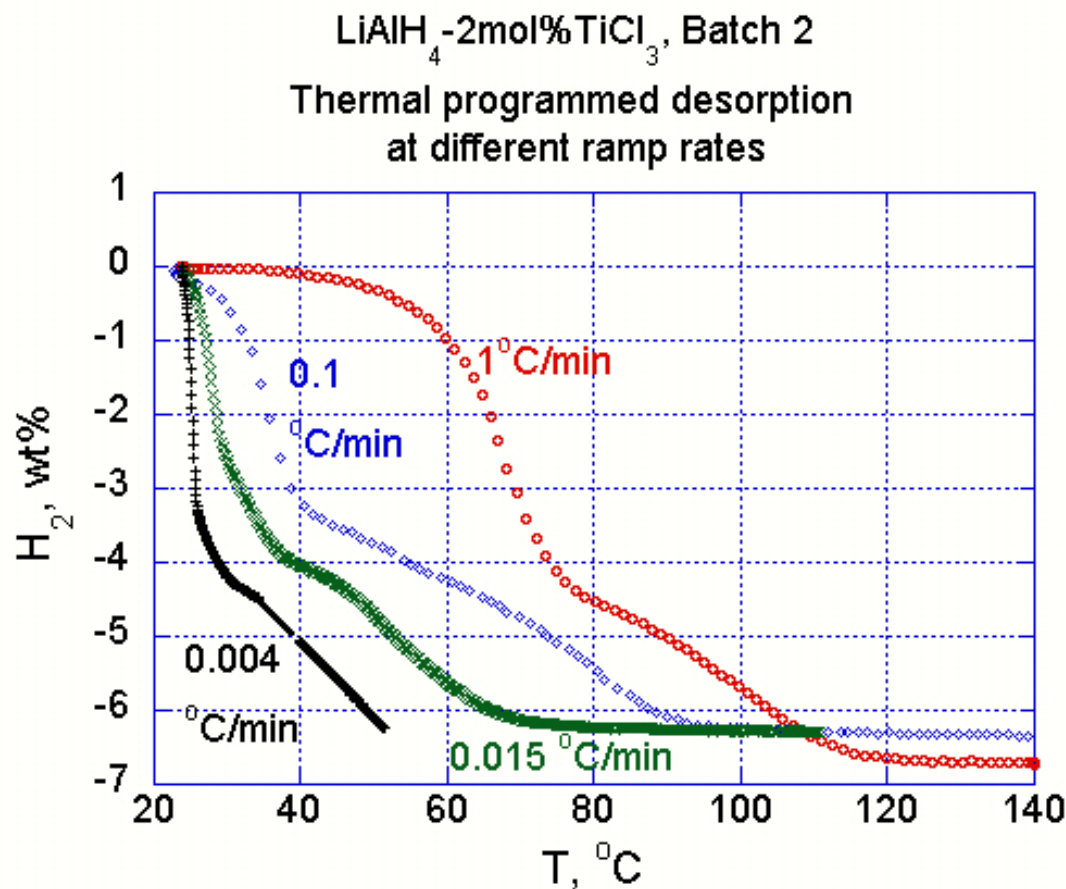


Additives increases temperature for conversion of  $\text{LiAlH}_4$  to  $\text{Li}_3\text{AlH}_6$

Temperature for release of  $\text{H}_2$  from  $\text{Li}_3\text{AlH}_6$  is not particularly dependent on level of additives or impurities

No evidence for release of hydrogen from borohydride salts

# Temperature for decomposition of both $\text{LiAlH}_4$ and $\text{Li}_3\text{AlH}_6$ is dependent on rate of temperature increase in temperature programmed thermal decomposition



## Chemistry of Liquid and Volatile Metal Borohydrides $\text{Al}(\text{BH}_4)_3$ , $\text{Ti}(\text{BH}_4)_3$ , and $\text{Zr}(\text{BH}_4)_4$

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Borohydride complexes of Al, Ti, and Zr have been shown to be precursors for the CVD of metal borides with the evolution of  $\text{H}_2$  as a by-product – formation of crystalline ceramic-like metal boride product requires much higher temperature

Complexes mentioned above are covalent molecular compounds with bridging M-H-B bonds

Volatile or liquid hydrogen storage material will have some engineering advantages for scale-up – heat and mass transfer

**Concept:** Volatile (or liquid)  $\text{M}(\text{BH}_4)_n$  transported to heated zone containing catalyst for hydrogen production, high pressure hydrogen in presence of catalyst regenerates storage compound

## Diborane reacts with LiAlH<sub>4</sub> in diethyl ether solvent

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Product distribution depends on the proportions in which reactants are combined



The Al containing product is a liquid

Ashby and Foster, *J. Am Chem Soc*, **1966**, 88, 3248.

### **Volatile and Liquid Metal Borohydrides:**

Preparation for solvent free materials

Design apparatus to study decomposition of volatile compounds

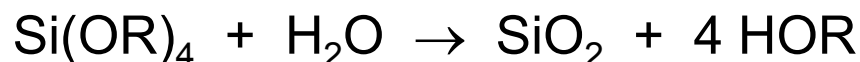
Set up mass spectrometer to analyze decomposition products (potential product is diborane, B<sub>2</sub>H<sub>6</sub>)



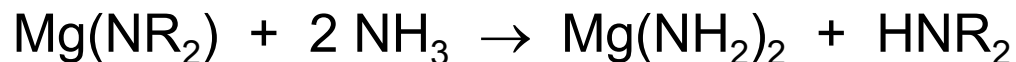
## Organic Amide/Ammonia Analog of Sol-gel Process

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Traditional sol-gel process: metal alkoxides react with water to form polymeric metal oxides and alcohol



Metal dialkylamides react with ammonia to form metal amide/imide and dialkylamine



Surfactants form micelles in liquid ammonia analogous to aqueous solution; inverted micelle provides method of limiting reaction to materials in ammonia “pocket;” controlled particle size

Inverted micelles in liquid ammonia poorly defined, investigation needed to determine appropriate surfactants and concentrations

# Technical Accomplishments

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Preparing amides (and imides or nitrides) of Li and Mg in liquid ammonia incorporating Ti catalyst as “ $Ti_3N_4$ ” using previously characterized product of the ammonolysis of  $Ti(NR_2)_4$  in liquid  $NH_3$

$LiNR_2$  and  $Mg(NR_2)$  where  $R = CH(CH_3)_2$  (isopropyl) are stable and soluble in dry hydrocarbon solvent

# Future Work

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Demonstrate that decomposition product of  $\text{TiR}_{(4-n)}(\text{AlH}_4)_n$  where R = alkyl or aryl, is an effective catalyst thermal for hydrogen uptake and release from alanates

## MHCoE Project B – Complex Anionic Materials (borohydrides, alanates)

Test Ti and Ti-Al catalysis of decomposition reaction of metal borohydrides; determine whether reaction is reversible

Decomposition of liquid  $\text{Al}(\text{BH}_4)_3$  in sealed tube

Preparation of  $\text{LiM}(\text{BH}_4)_4$  where M = Al, Ti by reaction of  $\text{M}(\text{BH}_4)_3$  with  $\text{LiBH}_4$  in solution

## MHCoE Project C – Amides/Imides (M-N-H systems)

Test Ti and Ti-Al catalysis of Li-Mg-N-H system when catalyst introduced as organic amide

Find surfactant-hydrocarbon combination for inverted micelle in ammonia

# Summary/Milestones

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## **MHCoE Project B:**

Synthesis of liquid and volatile metal borohydrides and characterization of thermal decomposition reactions in the vapor phase/liquid phase in presence of catalyst (Al-Ti) – Sept 30, 2007

Determine whether liquid or volatile materials can be effective for reversible hydrogen storage – Sept 30, 2007

## **MHCoE Project C:**

Develop general methodology for the preparation of metal amide/imides using organic amide/ammonia analog of sol-gel process and liquid ammonia techniques – March 31, 2007

**Percentage of effort in remainder of FY06 and FY07: 10-15% catalyzed alanates, 40-45% metal borohydride, 40-45% metal amide/imide (M-N-H)**