

# Carbon Aerogels for Hydrogen Storage

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**Hydrogen Sorption Center of Excellence  
DOE Hydrogen Program Annual Merit Review  
June 9, 2010**

**This presentation contains no confidential or proprietary information**

This work was performed under the auspices of the U.S. Department of Energy by  
Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

**Project ID:  
ST077**

# Project Overview

## Timeline

- Project start: FY05
- Project end date: FY10
- Percent complete: 100%

## Budget

- Total project funding (proposed): \$1050K
- Funding received in FY09: \$470 K
- Funding for FY10: \$302 K

## Technical Barriers Addressed by Project

- A. System Weight and Volume
- C. Efficiency
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

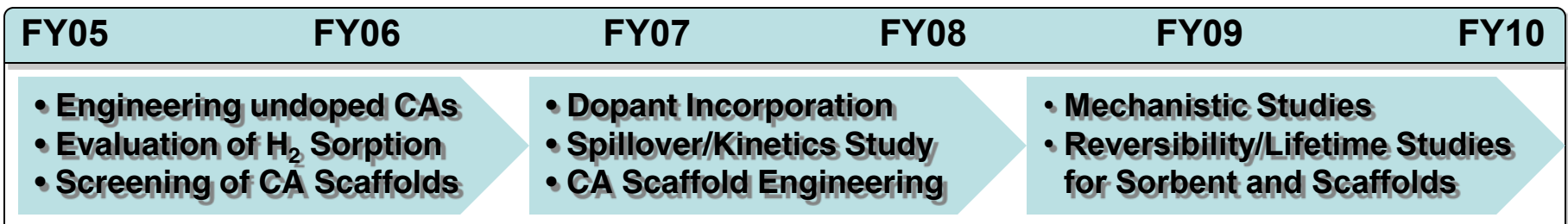
## Partners

- CalTech (Prof. Ahn)
  - H<sub>2</sub> adsorption measurements
- NIST (C. Brown)
  - MOF processing
- UNC-Chapel Hill (Prof. Wu)
  - Advanced NMR analysis
- HRL Laboratories (J. Vajo, MHCoe)
  - Scaffolds for Metal Hydrides



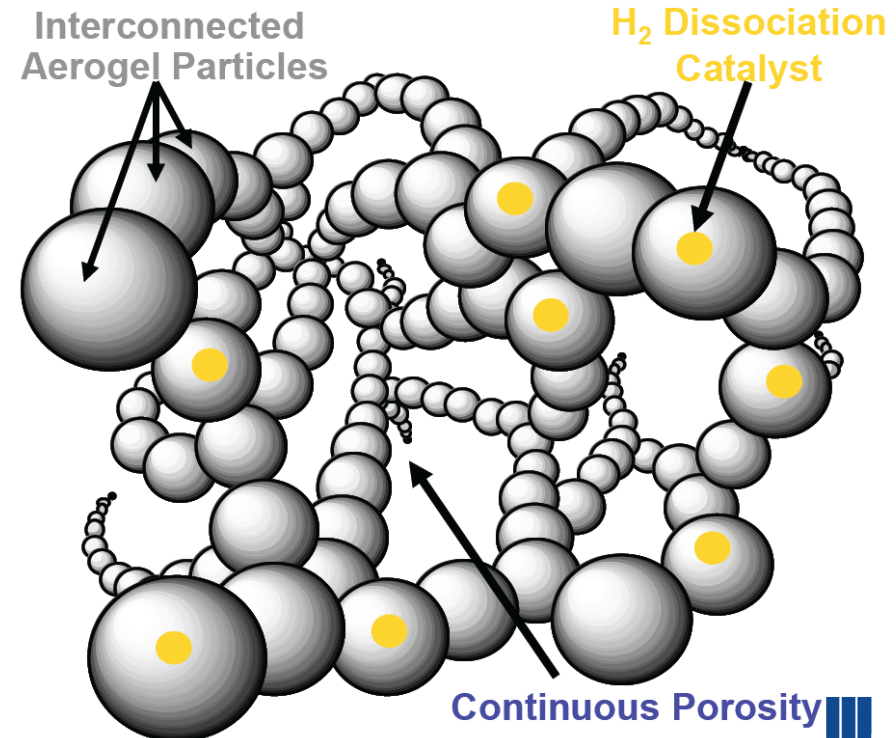
# Project Objectives

- Our objective is the design of novel aerogel materials that meet the DOE *system* targets (6 wt%, 45 g/L) for on-board vehicle H<sub>2</sub> storage
- Efforts were focused in two areas:
  - **Engineering of aerogel-based sorbent materials:**
    - Optimize structure for enhanced H<sub>2</sub> uptake and improved kinetics
    - Storage at reasonable operating temperatures
  - **Design of aerogel materials as porous scaffolds for light metal hydride systems:**
    - Potential to improve kinetic and thermodynamic performance of metal hydrides



# Project Approach-Part 1

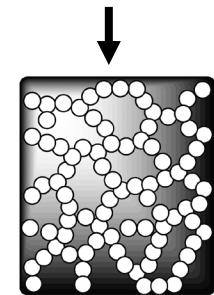
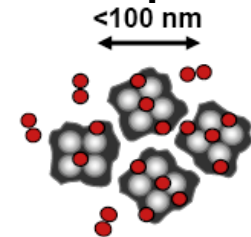
- Our approach is to utilize the flexibility of aerogel synthesis for the design new sorbent materials
- Aerogel synthesis allows for control over bulk properties (**surface area, pore size, pore volume, composition, density**) and for the homogeneous incorporation of modifiers (**metal catalysts, organometallic species**) into the matrix
- With this approach, we can control:
  - **Surface chemistry and microstructure** of the sorbent
  - **Dispersion** of the modifier (i.e. Pt nanoparticles for spillover)
- We can also use this flexibility to explore other sorbent materials with unique compositions
- Process is scaleable for production of monoliths or powders



# Project Approach-Part 2

- Improved reaction kinetics for reversible H<sub>2</sub> storage in complex metal hydrides can be achieved through use of nanoporous scaffolds
  - Limits particles sizes and reduces diffusion distances
- We are fabricating aerogels as scaffolds for light metal hydrides (LMH), such as MgH<sub>2</sub>, LiBH<sub>4</sub> and NaAlH<sub>4</sub>
  - Work with HRL Laboratories (Metal Hydride CoE)
- Structural requirements for practical application of MH scaffolds:
  - Large pore volumes (minimize capacity penalty)
  - Small pore sizes (limit particle sizes)
  - Good thermal conductivity
  - Compatible surface chemistry
- We are using the flexibility of aerogel synthesis to design novel nanocomposites that possess the requisite structural, chemical and transport properties for metal hydride scaffolding

MH Nanoparticles



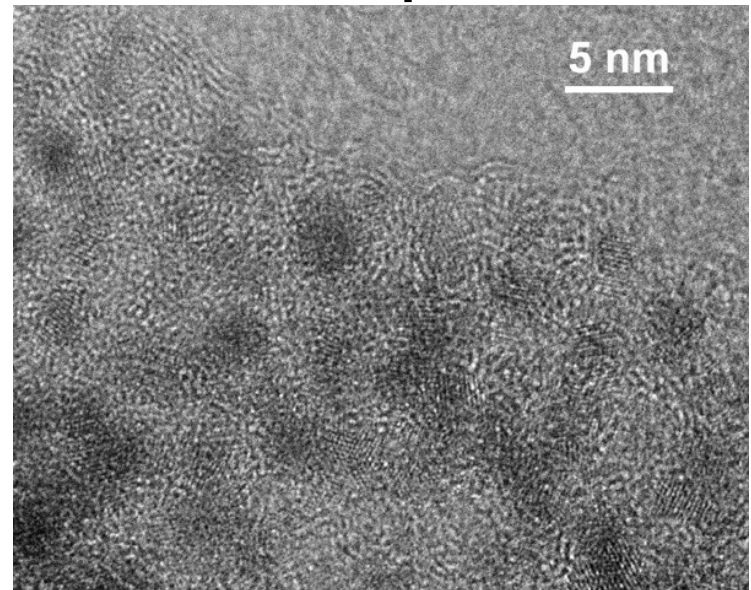
Porous Scaffold



# Previous Accomplishments:

## Activated CA Sorbents

- Microporous CAs with surface areas in excess of 3000 m<sup>2</sup>/g were prepared that exhibited surface excess H<sub>2</sub> adsorption of up to **5.3 wt%** and **29.2 g H<sub>2</sub>/L** at 77K
- These high surface area materials were used as supports for the design of new spillover materials with the goal of increasing overall H<sub>2</sub> capacity and improving uptake kinetics at room temperature
- Hydrogen dissociation catalysts (Ni, Pt) were incorporated into the aerogel supports by different methods to investigate the effects of catalyst dispersion and catalyst/support interface on H<sub>2</sub> uptake and kinetics
- Spillover systems derived from CAs exhibited significant issues with reproducibility for H<sub>2</sub> uptake at RT



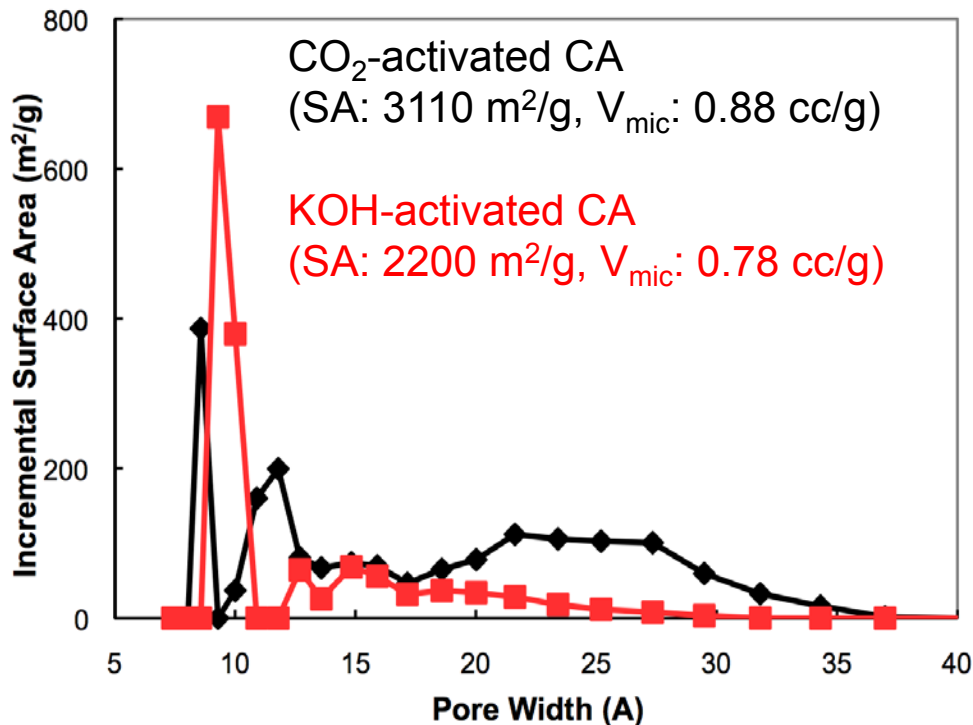
HR-TEM of Pt-doped ACA (2400 m<sup>2</sup>/g) prepared by atomic layer deposition





# Technical Accomplishments: Controlling Pore Size in Activated CAs

- New activated CAs have been prepared that exhibit higher bulk densities and increased micropore content:
  - Focus on increasing volumetric capacities in our ACAs
  - Improved textural properties achieved through modified thermal activation process
  - Smaller average pore sizes observed for KOH-activated CAs<sup>1</sup>



- Bulk densities of the high surface area ACAs is also improved
- Hybrid CO<sub>2</sub>-KOH activation process may provide access to ACA with desired pore structure
- Current target is an ACA with surface area ~2700 m<sup>2</sup>/g (> 5 wt% H<sub>2</sub>) that exhibits high bulk density (> 0.5 g/cc) and narrow micropore size distribution (< 10 Å)

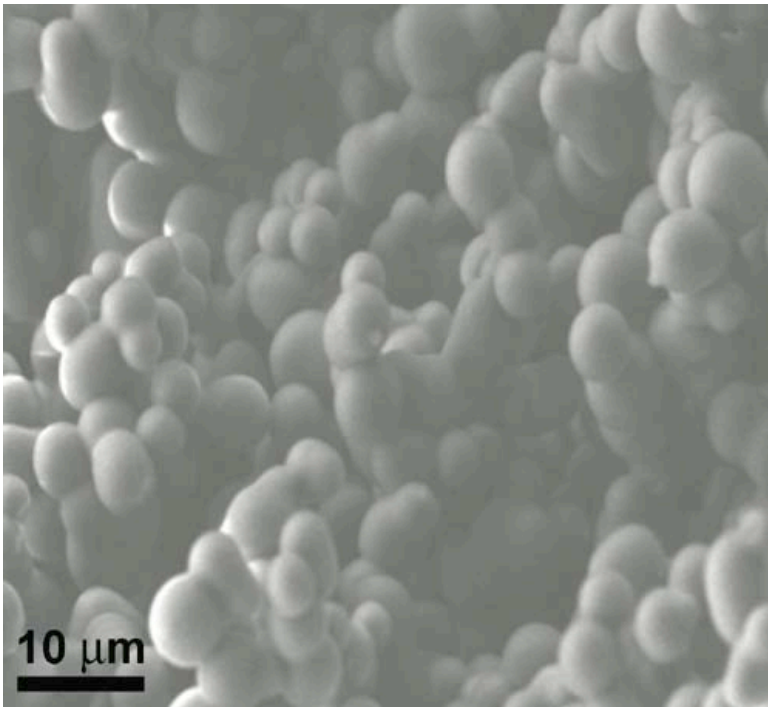
<sup>1</sup>Similar approaches have recently been reported: Meisner et al *Nanotech.* **2009**, 20, 204023; Wen et al *Electrochem. Comm.* **2009**, 11,715.



# Technical Accomplishments:

## New Spillover Receptors

- We have prepared new carbon aerogel materials derived from sugars that may have potential as spillover receptors:
  - Materials derived from carbonization of sucrose or glucose aerogels<sup>1</sup>
  - Carbonized sugar aerogels (cSA) are comprised entirely of “bridge” material used to enhance hydrogen uptake in other spillover systems<sup>2</sup>



**Carbonized Sucrose Aerogel**  
(BET SA: 400 m<sup>2</sup>/g)

- This material should exhibit very different surface characteristics than those of traditional activated carbons, especially with regard to oxygen-containing species
- Potential to improved kinetics of spillover process
- Current focus for cSAs:
  - Increasing surface area either through aerogel synthesis or thermal activation process
  - Incorporation of hydrogen dissociation catalysts (i.e. Ru)

<sup>1</sup> T. F. Baumann et al., *J. Mater. Chem.*, **2010**, submitted.

<sup>2</sup> Yang et al., *JACS*, **2006**, *128*, 8136.





# Previous Accomplishments: CA Scaffolds

- New CAs were prepared and tested as scaffolds with  $\text{LiBH}_4$ :
  - The 2<sup>nd</sup> generation materials combined the large pore volumes of the our 1<sup>st</sup> generation CAs with the small pore size of HRL xerogels



## 1<sup>st</sup> Generation

HRL Carbon Xerogel

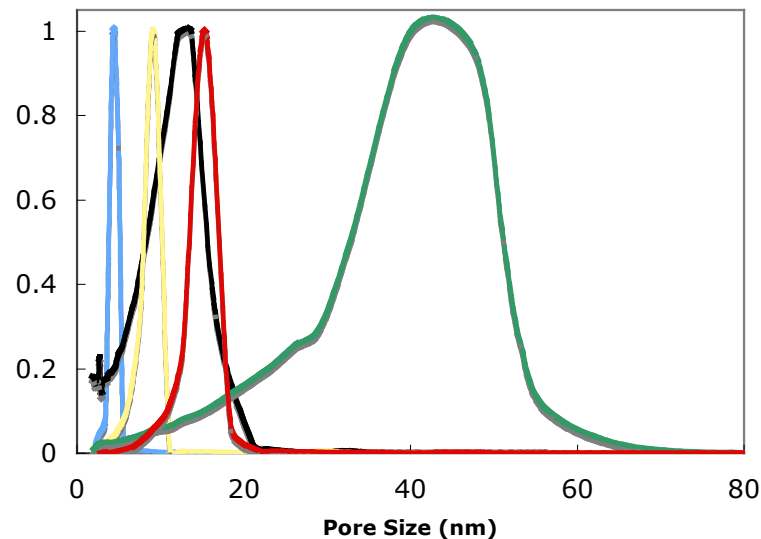
APD ~ 13 nm

PV = 1.1 cm<sup>3</sup>/g

LLNL CA

APD ~ 40 nm

PV = 2.7 cm<sup>3</sup>/g



## 2<sup>nd</sup> Gen Scaffolds

APD ~ 15 nm

PV = 2.6 cm<sup>3</sup>/g

APD ~ 9.5 nm

PV = 1.1 cm<sup>3</sup>/g

APD ~ 4 nm

PV = 0.5 cm<sup>3</sup>/g

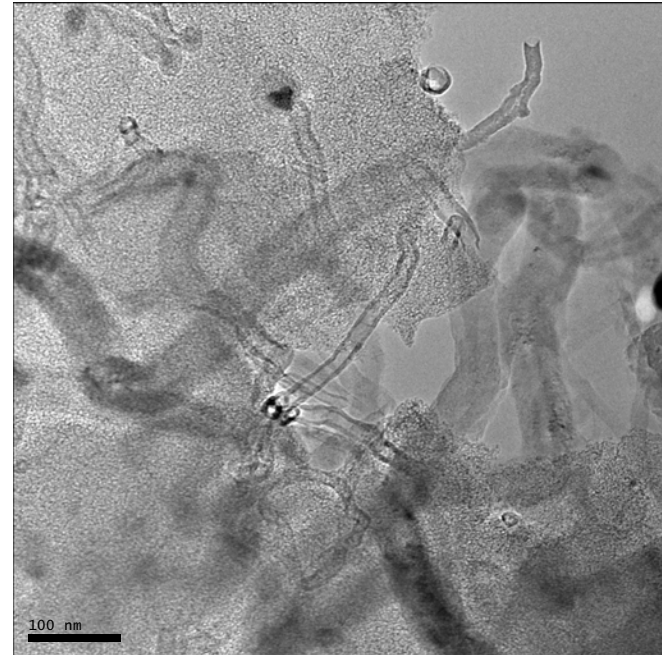
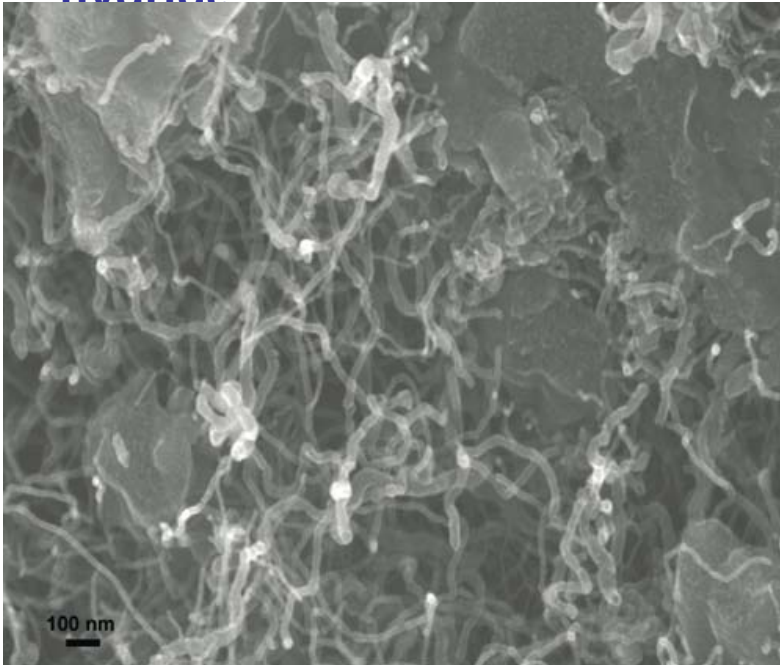
- $\text{LiBH}_4$  composites prepared with these scaffolds exhibited decreases in dehydrogenation temperatures relative to bulk  $\text{LiBH}_4$
- We also synthesized new carbon nanotube (CNT)-CA composites as next-generation scaffold materials:
  - Improved thermal transport in these scaffolds
  - CNTs appeared to influence hydrogen desorption process for  $\text{LiBH}_4$



# Technical Accomplishments:

## Carbon Nanotube-CA Composites

- We have developed a new method for growing CNTs directly in the pores of the CA scaffold:
  - CVD growth of multi-walled CNTs within metal-loaded CAs (M=Ni, Fe)
  - CNTs fill the open pore volume of the scaffold
  - Approach provides larger interfacial area between CNTs and metal hydride



**SEM and TEM images of MWCNTs grown in the pores of an ACA (2400 m<sup>2</sup>/g)**

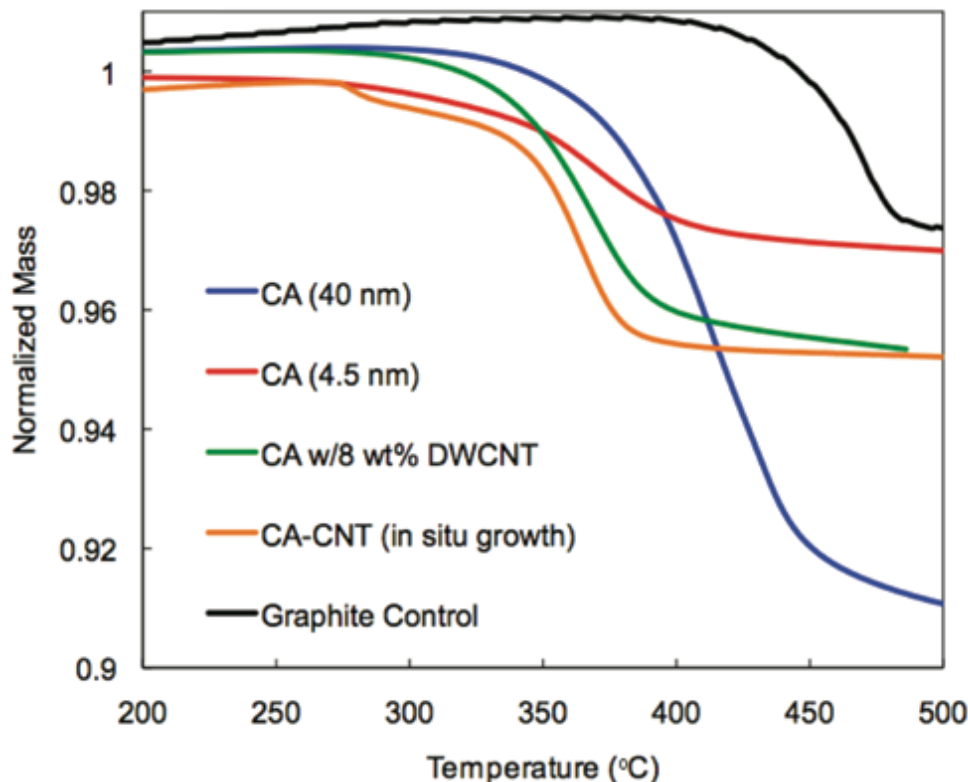


# Technical Accomplishments: Carbon Nanotube-CA Composites

- $\text{LiBH}_4$  composites prepared with these CA-CNT scaffolds exhibited lower dehydrogenation temperatures than either the bulk hydride or composites made with the smaller pore CA scaffolds



TGA data for  $\text{LiBH}_4$  incorporated into different CA scaffolds



- Dehydrogenation temperature is lower than expected based on the large average pore size of the CA-CNT scaffold (>100 nm)
- Interaction of  $\text{BH}_4$  with CNT surface may influence rate of  $\text{H}_2$  exchange, similar to the effect reported for  $\text{LiAlH}_4/\text{CNT}$  systems<sup>1</sup>
- Metal catalyst nanoparticles (Ni) may also play role in dehydrogenation process

<sup>1</sup>P. A. Berseth, *et al.*, *Nano Letters*, **2009**, 9, 1501.

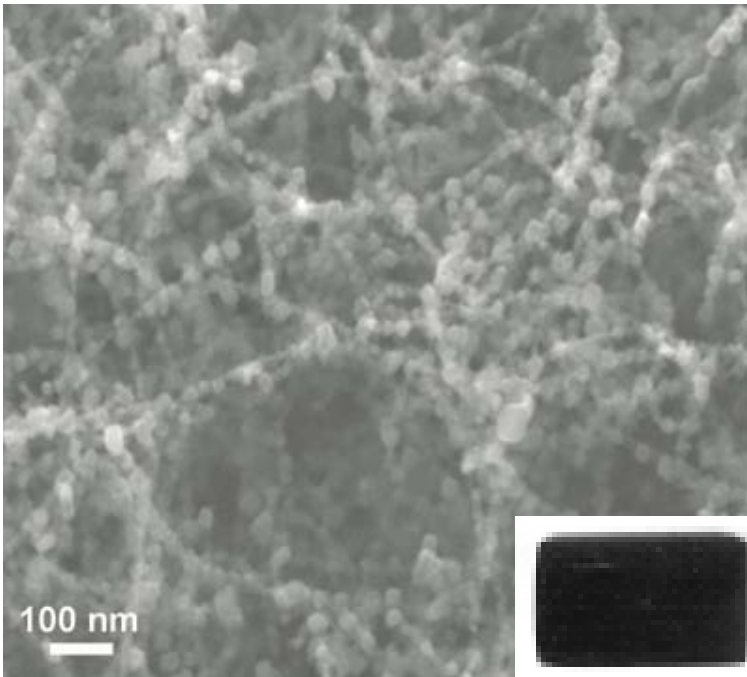
Weight losses indicate dehydrogenation and scale with  $\text{LiBH}_4$  loading



# Technical Accomplishments:

## Surface Modification of Scaffolds

- We have also developed methods<sup>1</sup> for preparing monolithic scaffolds with surface coatings that are inert and can improve the wetting characteristics of the scaffold for magnesium metal:
  - Metal carbide surfaces (i.e TiC) have been shown to exhibit better wetting compatibility with Mg than pure carbon surfaces<sup>2</sup>
  - CA scaffolds coated with a uniform layer of TiC have been prepared



SEM image and photograph (part ~2 cm) of a TiC-coated CNT-CA scaffold

- These materials are prepared by a simple two-step process:
  - The scaffold is first coated with a thin layer of TiO<sub>2</sub> using either vapor- or solution-phase techniques
  - The TiO<sub>2</sub>-CA is then treated at 1400°C under Ar, leading to carbothermal reduction of the TiO<sub>2</sub>
- This approach allows for coating of the surfaces of the scaffold without compromising pore volume

<sup>1</sup>Worsley, et al., *J. Mater. Chem*, **2009**, 19, 7146 and *J. Mater. Chem.* **2009**, 19, 5503.

<sup>2</sup>Levi, et al., *Acta Mater.* **1999**, 47, 3927.



# Collaborations

## • Partners:

- **CalTech (Academic):** H<sub>2</sub> uptake measurements in spillover materials as well as new sorbent systems
- **HRL Laboratories (Industry):** Evaluation of aerogels as scaffolds for metal hydrides
- **NREL (Federal):** (1) Performance evaluation of new spillover materials and (2) testing of functionalized aerogels as supports for organometallic species
- **NIST (Federal):** (1) Supercritical processing of MOF sorbents and (2) evaluation of scaffolding effects on performance of metal hydride materials by Neutron Scattering experiments
- **UNC-Chapel Hill (Academic):** Advanced NMR analysis of H<sub>2</sub> sorption in high surface area sorbents



# Future Work

- **Complete work on modified synthesis/activation process to increase volumetric capacities of ACA:**
  - Hybrid activation to control evolution of micropores
  - Improved architecture to increase bulk density
- **Evaluate performance of new sugar-based spillover receptor:**
  - Test spillover behavior (uptake, kinetics, reversibility) in metal-doped cSAs
- **Optimize CNT-CA scaffolds for metal hydrides:**
  - Continued engineering of scaffold structure (porosity, CNT-loading)
  - Modify surface chemistry of the scaffolds to improve MH wetting behavior
  - Incorporation of catalysts/destabilizing agents into CA-CNT composites





# Project Summary

**Relevance:** Design of new aerogel materials for hydrogen storage

**Approach:** Incorporation of modifiers into high surface area aerogels to maximize H<sub>2</sub> uptake and increase binding energies

**Technical Accomplishments:**

- Improved pore size distribution in activated CAs
- Fabricated new spillover receptors derived from sugars
- Prepared novel CA-CNT nanocomposites as scaffolds for metal hydride systems

**Center Collaborations:**

- Prof. Channing Ahn (CalTech): H<sub>2</sub> sorption measurements
- John Vajo (HRL, MHCoe): CA scaffolds for metal hydrides
- Craig Brown (NIST): (1) Supercritical processing of MOFs and (2) Characterization of CA structure by NS techniques
- Prof. Yue Wu (UNC): Characterization of CA structure and H<sub>2</sub> uptake by advanced NMR techniques



# Summary for CA Materials

## DOE On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 <i>System</i> Target	CA <i>Material</i> Results
Specific Energy	kWh/kg (wt% H <sub>2</sub> )	2.0 (6 wt% H <sub>2</sub> )	5.3 wt% at 77 K and 30 bar
Energy Density	kWh/L (g H <sub>2</sub> /L)	1.5 (45 g H <sub>2</sub> /L)	~29 g H <sub>2</sub> /L

