Carbon Aerogels for Hydrogen Storage

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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_2 adsorption measurements
- NIST (C. Brown)
  - MOF processing
- UNC-Chapel Hill (Prof. Wu)
  - Advanced NMR analysis
- HRL Laboratories (J. Vajo, MHCoE)
  - Scaffolds for Metal Hydrides

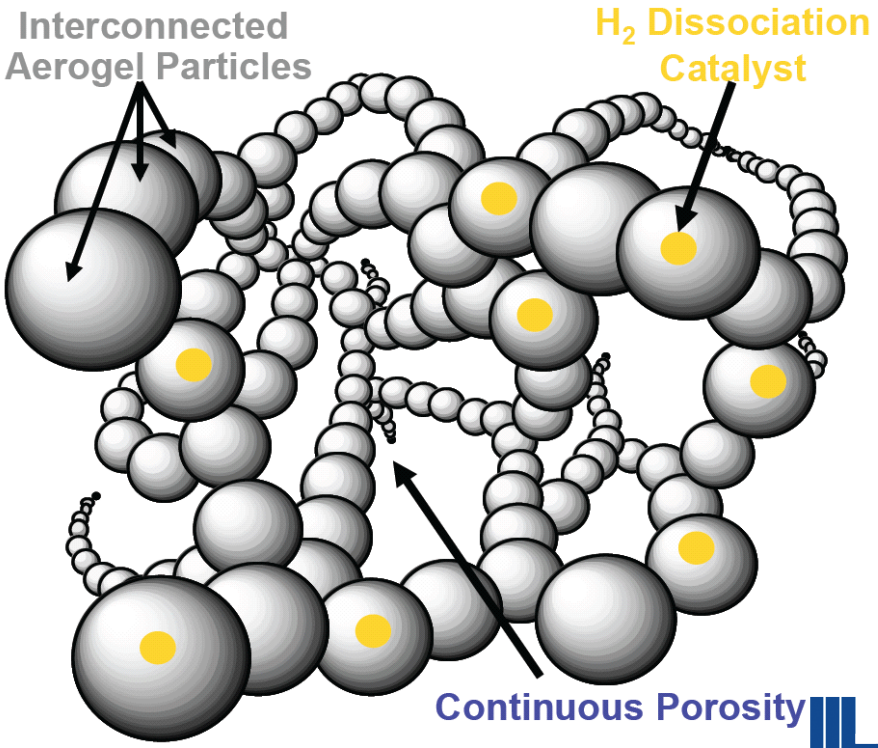
Project Objectives

- 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_2 storage
- Efforts were focused in two areas:
  - Engineering of aerogel-based sorbent materials:
    - Optimize structure for enhanced H_2 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

FY05	FY06	FY07	FY08	FY09	FY10
• Engineering undoped CAs • Evaluation of H_2 Sorption • Screening of CA Scaffolds		• Dopant Incorporation • Spillover/Kinetics Study • CA Scaffold Engineering		• Mechanistic Studies • Reversibility/Lifetime Studies for Sorbent and Scaffolds	

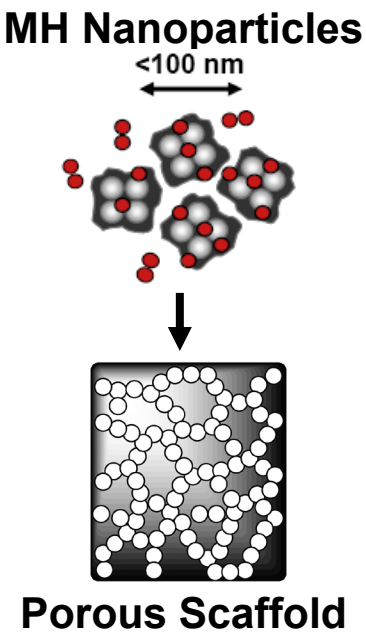
Project Approach-Part 1

- 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

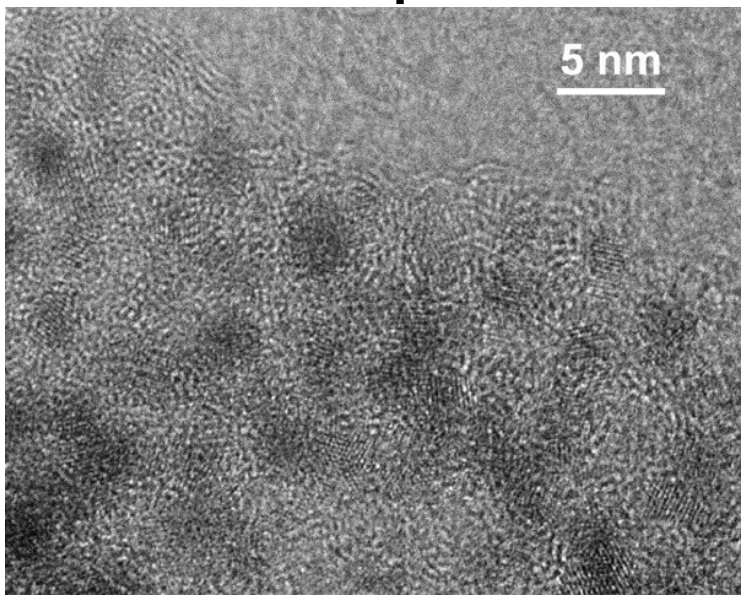
- Improved reaction kinetics for reversible H_2 storage in complex metal hydrides can be achieved through use of nanoporous scaffolds
  - Limits particles sizes and reduces diffusion distances
- We are fabricating aerogels as scaffolds for light metal hydrides (LMH), such as MgH_2, $LiBH_4$ and $NaAlH_4$
  - 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

Previous Accomplishments:
Activated CA Sorbents

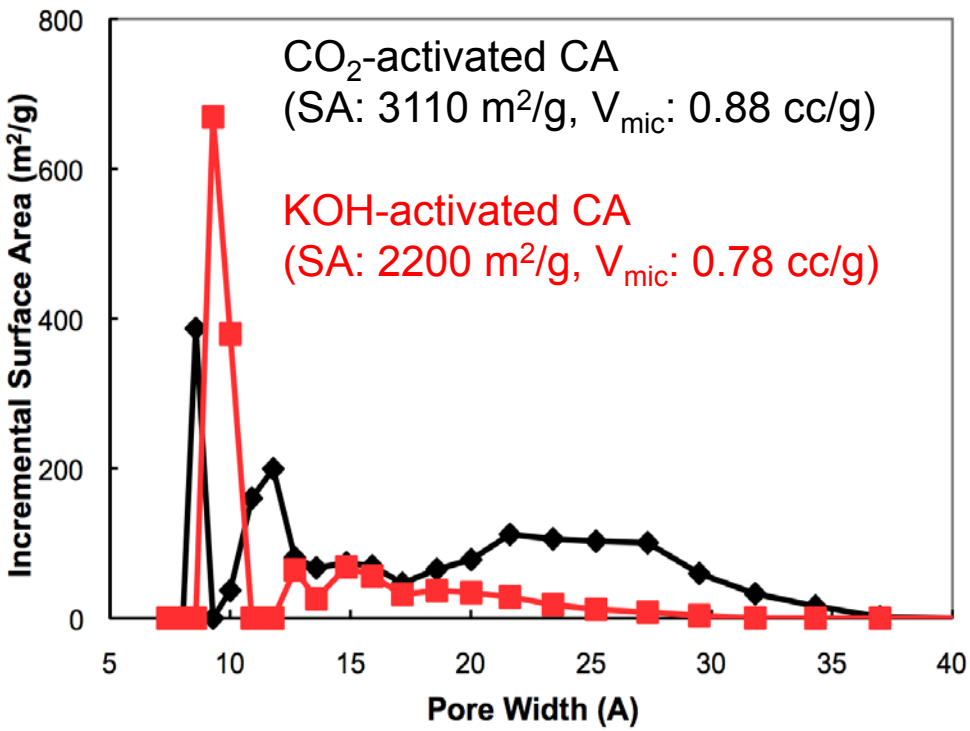
- Microporous CAs with surface areas in excess of 3000 m^2/g were prepared that exhibited surface excess H2 adsorption of up to 5.3 wt% and 29.2 g H_2/L at 77K
- These high surface area materials were used as supports for the design of new spillover materials with the goal of increasing overall H_2 capacity 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_2 uptake and kinetics
- Spillover systems derived from CAs exhibited significant issues with reproducibility for H_2 uptake at RT



HR-TEM of Pt-doped ACA (2400 m^2/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[1]**

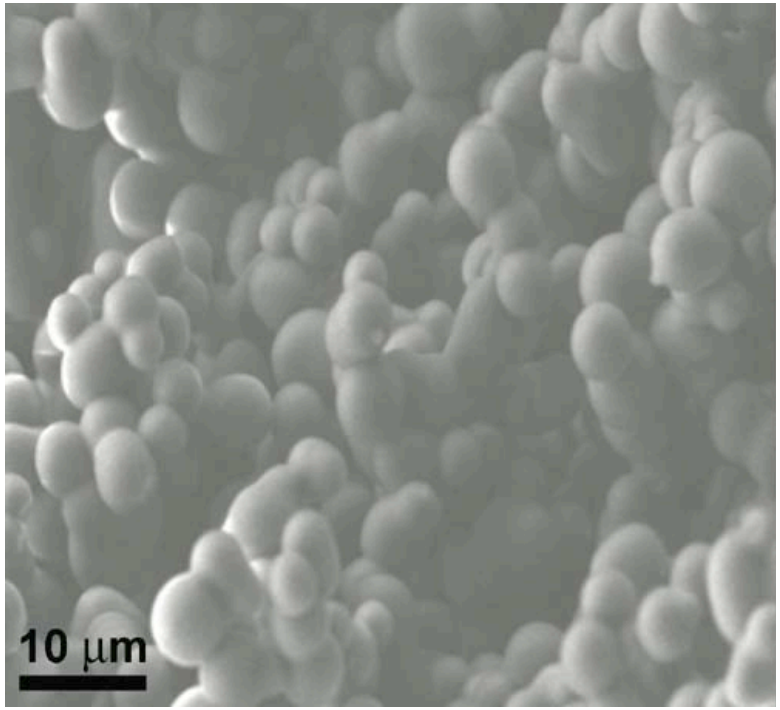


- **Bulk densities of the high surface area ACAs is also improved**
- **Hybrid CO_2-KOH activation process may provide access to ACA with desired pore structure**
- **Current target is an ACA with surface area ~2700 m^2/g (> 5 wt% H_2) that exhibits high bulk density (> 0.5 g/cc) and narrow micropore size distribution (< 10 Å)**

[1]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[1]**
  - **Carbonized sugar aerogels (cSA) are comprised entirely of "bridge" material used to enhance hydrogen uptake in other spillover systems[2]**



Carbonized Sucrose Aerogel (BET SA: 400 m^2/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)**

[1] T. F. Baumann et al., *J. Mater. Chem.*, **2010**, submitted.
[2] Yang *et al.*, *JACS,* **2006***, 128,* 8136.

Previous Accomplishments:
CA Scaffolds

- **New CAs were prepared and tested as scaffolds with $LiBH_4$:**
  - **The 2nd generation materials combined the large pore volumes of the our 1st generation CAs with the small pore size of HRL xerogels**

METAL HYDRIDE CENTER OF EXCELLENCE

1st Generation
HRL Carbon Xerogel
APD ~ 13 nm
PV = 1.1 cm^3/g

LLNL CA
APD ~ 40 nm
PV = 2.7 cm^3/g

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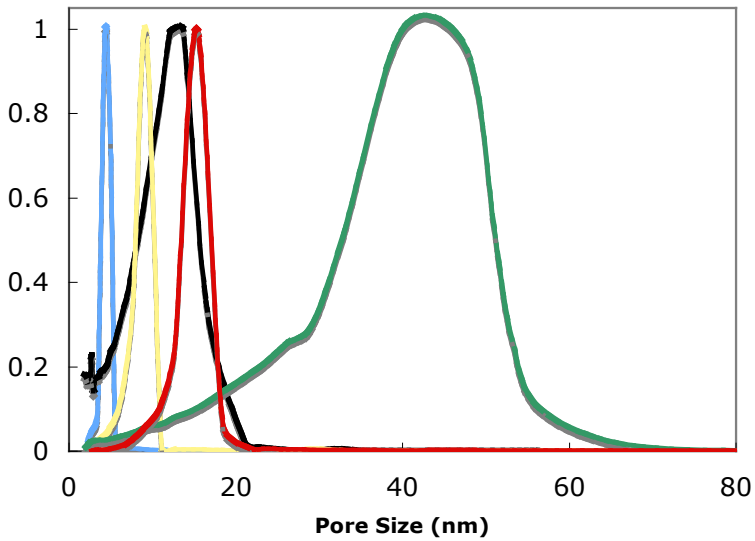


2nd Gen Scaffolds
APD ~ 15 nm
PV = 2.6 cm^3/g

APD ~ 9.5 nm
PV = 1.1 cm^3/g

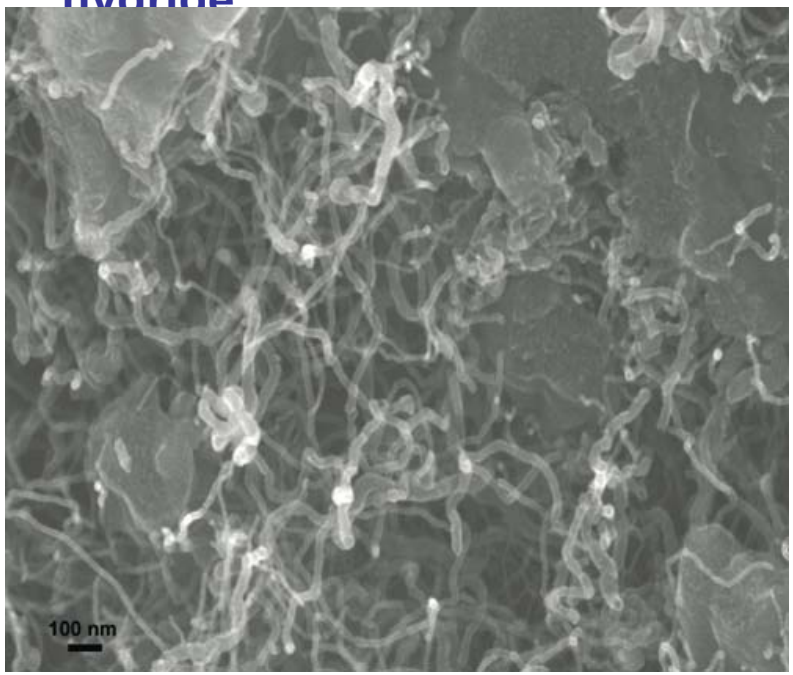
APD ~ 4 nm
PV = 0.5 cm^3/g

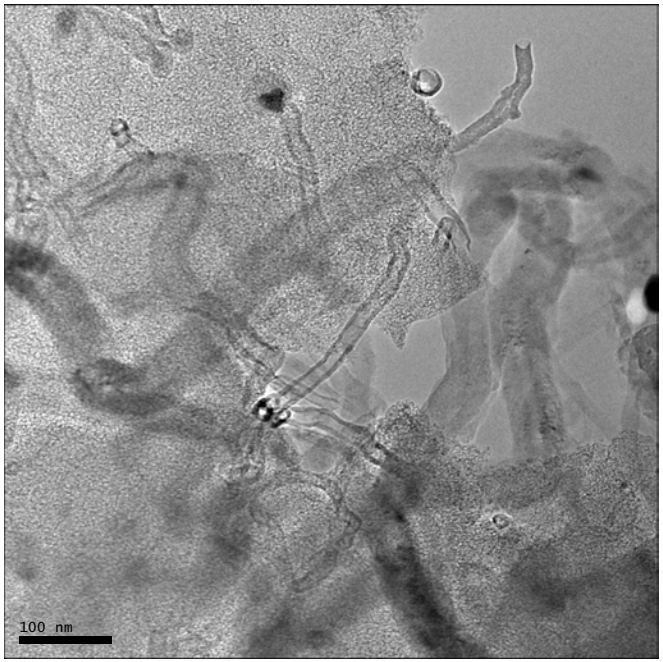
  - **$LiBH_4$ composites prepared with these scaffolds exhibited decreases in dehydrogenation temperatures relative to bulk $LiBH_4$**

- **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 $LiBH_4$**

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^2/g)

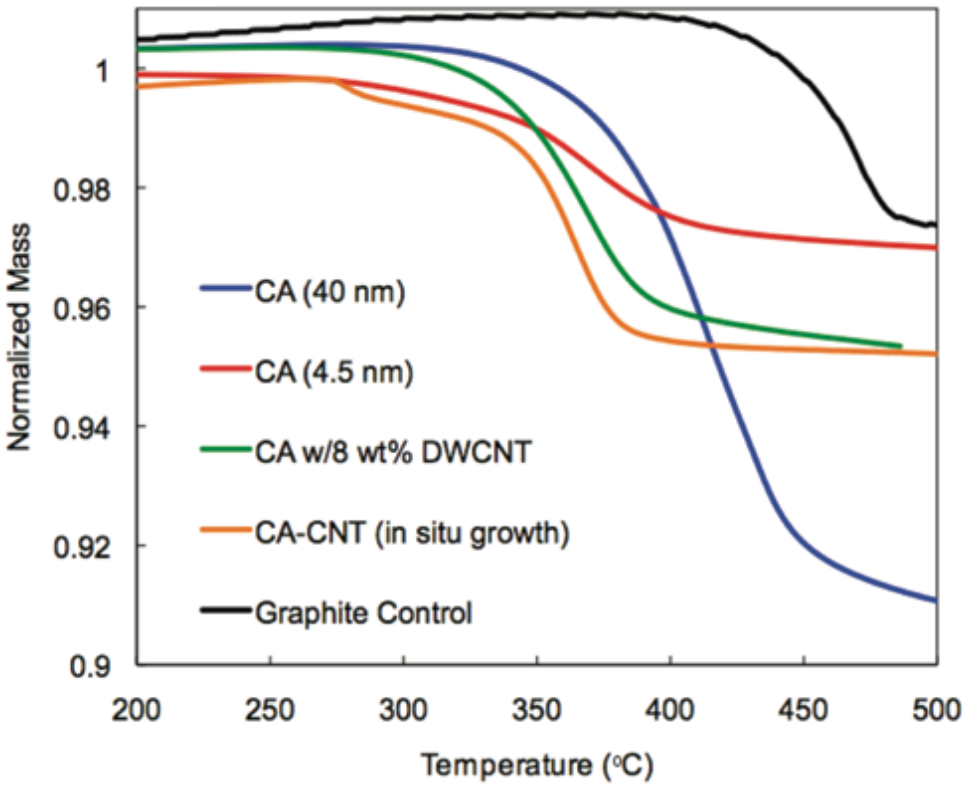
[1]M. A. Worsley, J. H. Satcher, Jr. and T. F. Baumann, *Langmuir*, **2010**, submitted.

Technical Accomplishments:
Carbon Nanotube-CA Composites

- **$LiBH_4$ 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**

HRL LABORATORIES

TGA data for $LiBH_4$ incorporated into different CA scaffolds



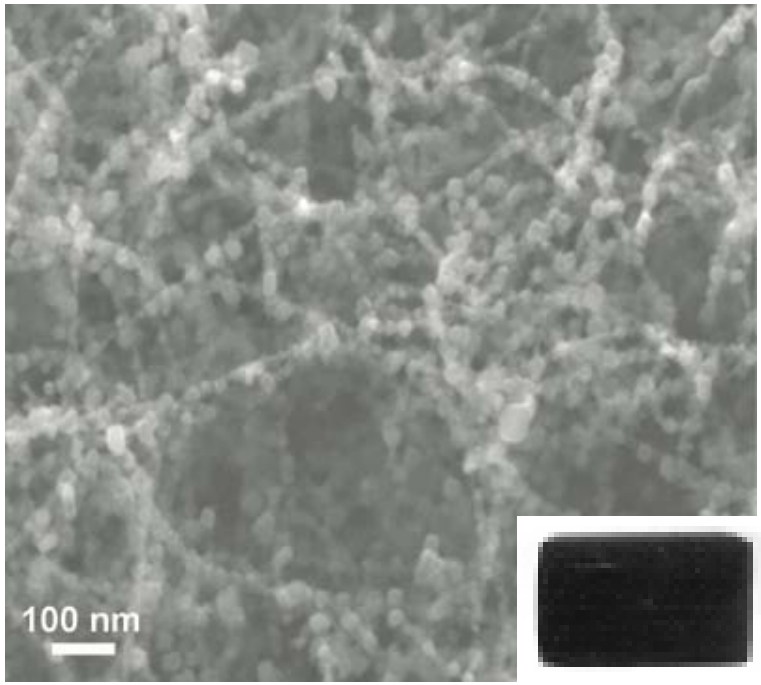
Weight losses indicate dehydrogenation and scale with $LiBH_4$ loading

- **Dehydrogenation temperature is lower than expected based on the large average pore size of the CA-CNT scaffold (>100 nm)**
- **Interaction of BH_4 with CNT surface may influence rate of H_2 exchange, similar to the effect reported for $LiAlH_4$/CNT systems[1]**
- **Metal catalyst nanoparticles (Ni) may also play role in dehydrogenation process**

[1]P. A. Berseth, *et al.*, *Nano Letters*, **2009**, *9*, 1501.

Technical Accomplishments:
Surface Modification of Scaffolds

- **We have also developed methods[1] 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[2]**
  - **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_2 using either vapor- or solution-phase techniques**
  - **The TiO_2-CA is then treated at 1400°C under Ar, leading to carbothermal reduction of the TiO_2**
- **This approach allows for coating of the surfaces of the scaffold without compromising pore volume**

[1]Worsley, *et al.*, *J. Mater. Chem*, **2009**, *19*, 7146 and *J. Mater. Chem.* **2009**, *19,* 5503.
[2]Levi, *et al.*, *Acta Mater.* **1999**, *47*, 3927.

Collaborations

- **Partners:**
  - **CalTech (Academic): H_2 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_2 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_2 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_2 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_2 uptake by advanced NMR techniques

Summary for CA Materials

DOE On-Board Hydrogen Storage System Targets

Storage Parameter	Units	2010 *System* Target	CA *Material* Results
Specific Energy	kWh/kg (wt% H_2)	2.0 (6 wt% H_2)	5.3 wt% at 77 K and 30 bar
Energy Density	kWh/L (g H_2/L)	1.5 (45 g H_2/L)	~29 g H_2/L