Richard E. Smalley Institute
For Nanoscale
Science and Technology
at Rice University

Nanoengineered Graphene Scaffolds with atom substitution for H_2 adsorption

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

Project ID #ST076: Tour

(Cloning Single Wall Carbon Nanotubes for Hydrogen Storage)

Overview

Timeline

- Start-Feb 2005
- Finish-June 2010
- 96% complete

Budget

- Total project funding (update)
- DOE share $1,765,989
- Contractor share $441,497
- Funding for FY07- $300,000
- Funding for FY08- $400,000
- Funding for FY09- $515,989
- Funding for FY10- $0

Barriers

General

A. Cost
B. Weight and Volume
C. Efficiency
D. Durability
E. Refueling Time

Reversible Solid-State Material

P. Lack of Understanding of H_2 Physi- and Chemisorption

Partners

NREL (L. Simpson),
Caltech (C. Ahn)
Oak Ridge NL (D. Geohegan)
Air Products (A. Cooper),
Penn State (M. Chung),
Rice U. (B. Yakobson)

DOE 2010 Targets for Storage System

- Gravimetric 45 g H_2/kg
- Volumetric 28 g H_2/L

Relevance: Objectives

The primary objective is to design and produce nanoengineered sp^2 atom-substituted carbon media that addresses the key technical barriers.

- >4.5wt% gravimetric uptake of hydrogen
- >45 g/L Volumetric uptake
- **Superior thermal management**: Fibrous media made from material with superb thermal conductivity compared to powders or granulated media. (~15kJ/mol & 2kg/min fill rate → 250kW heat removal)
- **High energy efficiency**: Lowest possible ΔS, hence lowest $-\Delta H$ for <10% energy loss, less heating when filled. Optimize binding energies with
- **Unrestricted kinetics**: Little or no activation barrier for adsorption, engineered H_2 gas channels in fiber
- **Thousand fill cycles**: No material fatigue using rigid slit pores.
- **Cost target of \$67/kg H_2:** Low cost precursor graphite and chemicals; Materials cost ~\$15/kg H_2 + common industrial fiber spinning process.
- **Media density ≥1g/cc**: Volumetric capacity tracks ahead of gravimetric capacity; these two targets are not in conflict.
- **Avoid extreme temperature swings**: Pure physisorption into uniform nanoengineered pores means that all adsorbed H_2 are equivalent, yielding the smallest temperature change with >95% delivery.
- **Understand all forces of attraction** for the molecular hydrogen in the pore.

Milestones 2010

Month/Year	Milestone
May-09	Demonstrate spinning process to make graphene fibrous media similar to CNT fiber (done)
Aug-09	Develop scalable synthetic methods for making graphene (done)
Sept-09	Downselected Pd nanoparticles as mobile catalyst for H-atom uptake
Nov-09	Adapt scalable methods for producing boron atom substituted graphene & followed by high substitution levels for nitrogen, and phosphorous. (done)
Jan-10	Test hydrogen uptake on atom substituted graphene, B, N, P (successful and ongoing)
Feb-10	Test for enhance binding energy of atom substituted graphene (successful and ongoing)
March-10	Develop templated growth of atom-substituted graphene on nanoparticles (successful and ongoing)
May-10	Develop proppants and functionalization for atom-substituted graphene to make engineered nanospaces with the modified graphene for enhanced H_2 uptake.

Milestones represent many experiments converging to an atom substituted graphene media with enhanced binding energy; which also provides an abundance of "parking spots" for metal atoms in a nanoengineered scaffold for near-ambient uptake of H_2

Approach -- overall

In the beginning: H_2 adsorption on pure Single Wall Carbon Nanotubes. No-go at end of phase I. Met all objectives, but had no control on pore sizes, which are generally too small.

Phase II Redirect: Engineered sp^2 carbon nanospaces with expanded and propped SWNTs. Spun as fibrous media rather than granular media**.**

Demonstrated enhanced uptake for H_2 in sp^2 nanopores

Expanded project to include graphene for sp^2 carbon "the new kid on the block", a material not available at beginning of this project.

Prop open graphene sheets to make engineered nanospaces & develop fiber spinning methods for and graphene nanoribbons; transfer expertise in functionalization and crosslinking of CNT to graphene (Earlier SWNT work and graphene compared)

Develop new synthetic methods and exploit sources of graphene as new low cost slit-pore nanoporous media.

Develop general synthetic methods for atom substituted graphene

Test hydrogen uptake in synthetic graphene and atom substituted graphene

Move towards increased binding energy with atom substituted and functionalized graphene.

The combination of sp^2 nanopores that provide enhanced uptake per unit SA, a high density media, and abundant sites for metal atom functionalization will lead to a media that will have the capability of exceeding DoE 2015 volumetric goals, close to RT.

Approach: graphene as low cost media

Develop a 5-step continuous spinning process to make the thermally conducting fibrous storage media for hydrogen uptake at near ambient temperature.

1. Prepare graphene from graphite
2. Make the spinning dope with pre-functionalized pyridine or amine binding sites
3. Spin graphene fibers from functionalized graphene
4. Pass through crosslinking bath, like sizing in reverse, making fiber porosity permanent.
5. Pass the "anti-sized" nanoporous fiber through ammonia bath to intercalate sodium

Array fibers into cables or woven fabric for hydrogen storage media with excellent thermal conductivity and gas flow. (Engineering step)

Cost estimate: Raw materials, per tonne
Sulfuric acid and ammonia solvents will be substantially recovered & taken into account.

1000kg	Graphite	$550/T
2000kg	Sulfuric acid	$100/T
500kg	Nitric acid (oxidizer)	$210/T
100kg	Ammonia	$200/T
200kg	Pyridine	$1000/T
100kg	Metallic sodium	$500/T
30kg	Methylene di-aniline	$2.50/kg

Total = $1370/T or $13.70 per 10 kg, to store 1 kg H_2 @ 9wt%

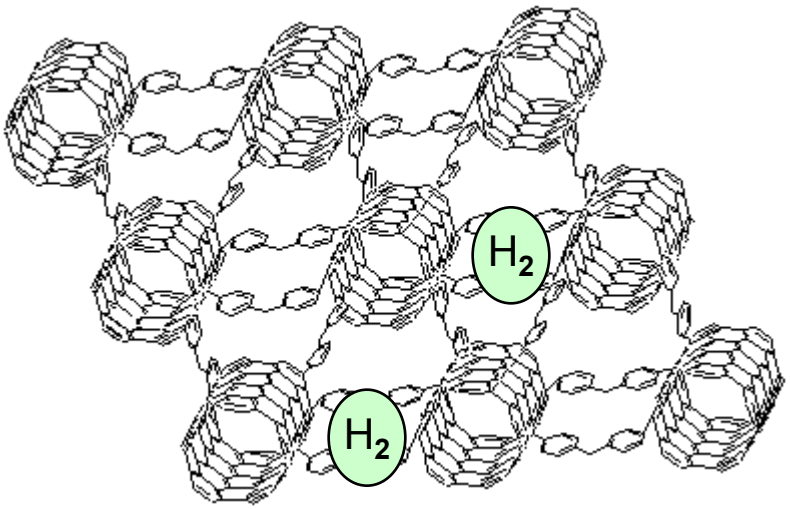
$1 kg to $3 kg for spinning and processing. Media cost $25 to $45 for 1 kg H_2 capacity, about half of $67/kg H_2 capacity (2015 target)

Using a media designed for fill pressure about 1/10 of compressed H_2 gas, & >2x greater capacity, this leads to a much lower unit cost pressure tank per kg H_2 stored.

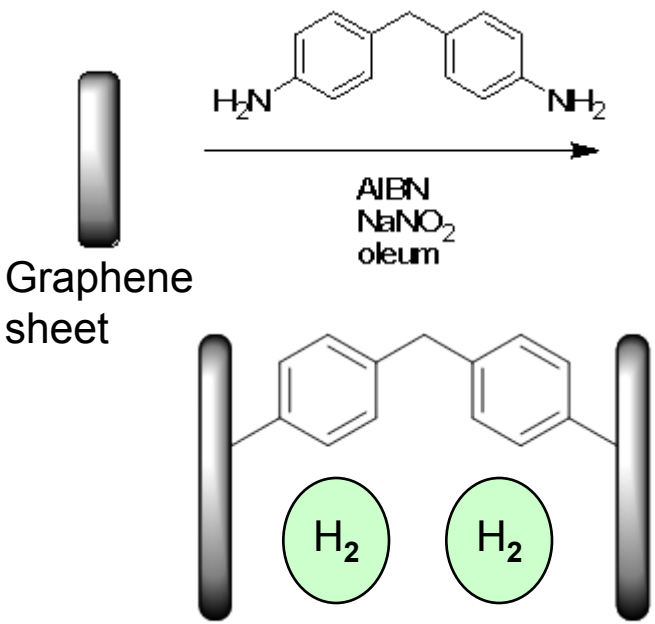
Approach: Engineered nanospaces of sp^2 carbon scaffold

<u>Nanoengineering:</u>

Developed methodology to made these nanostructured materials possible, with adjustable pore sizes needed for maximum hydrogen storage capacity.
The cross-linker determines the pore size. Technology of expansion and crosslinking developed for SWNT and transferred to graphene. SWNT and graphene fibers on next slide



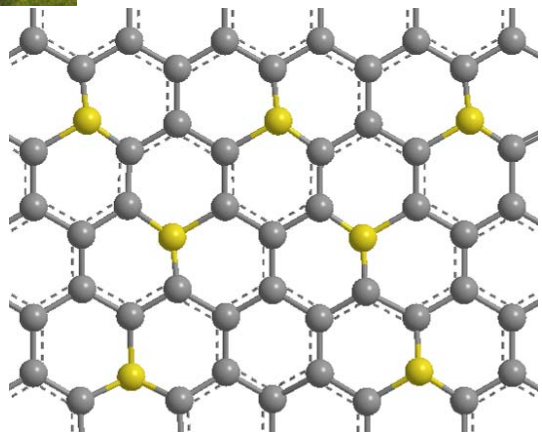
The nanotube rigid space frame scaffold
Using a diphenylmethyl linker.
Published JACS 131 (2), 723-728 (2009)



SWNT Scaffold concept developed in collaboration with Boris Yakobson, Rice University, HSCoE partner

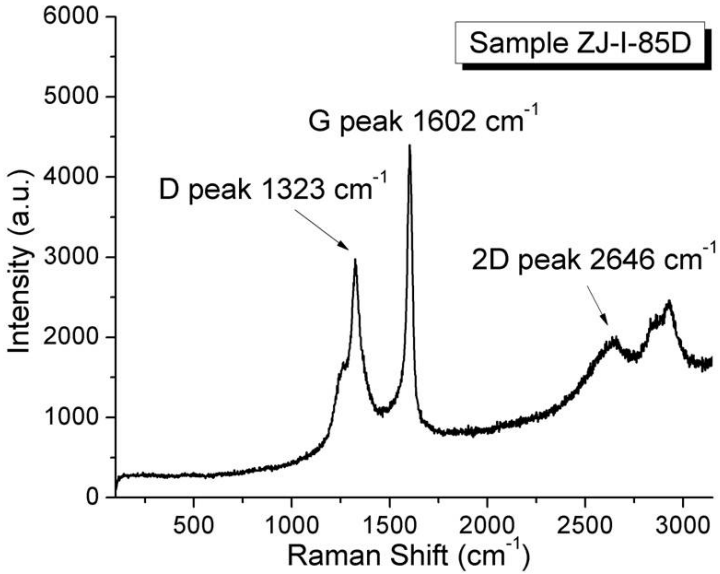
- Crosslinked SWNTS or graphene surrounds physisorbed H_2 with an sp^2 hybridized pi cloud
- Scaffolds enhance H_2 binding with atom substitution and can provide support for metal atoms
- Unlimited cycling does not degrade rigid nanoengineered scaffold

Accomplishment: Graphene with Boron Substitution

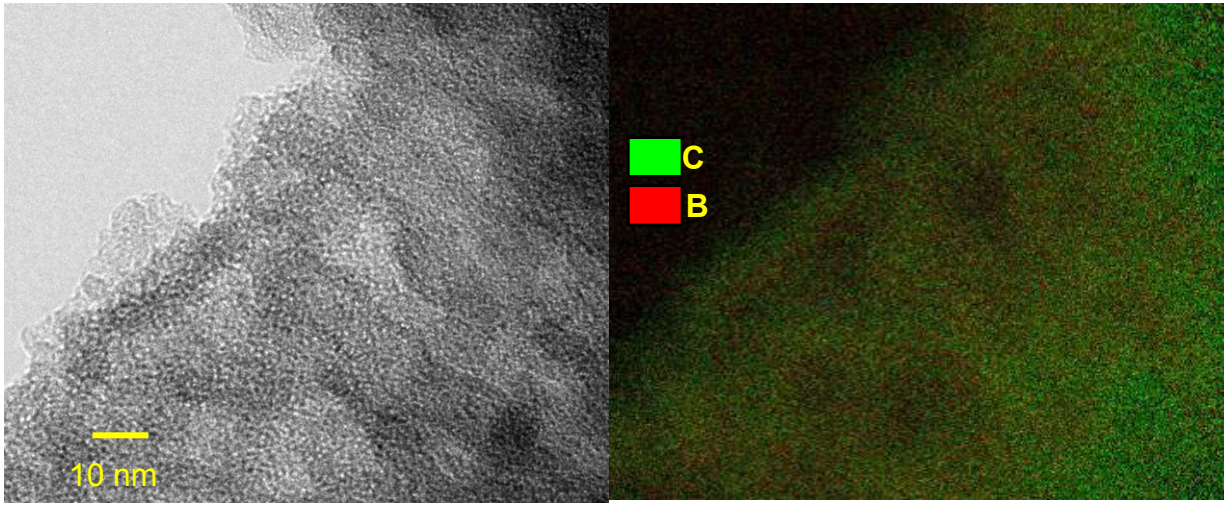


Carbon Boron substitution

Boron substitution concept from collaboration with Mike Chung at Penn State, HSCoE partner



Raman spectra of synthetic graphene with boron

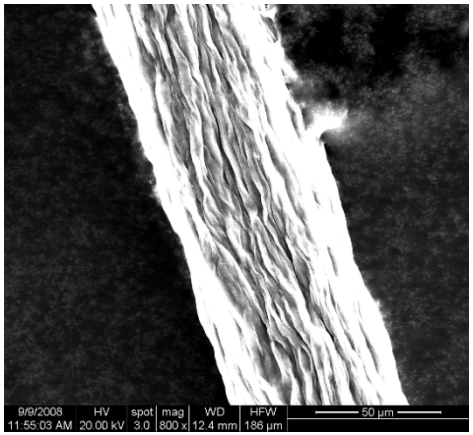


6% atom boron content determined by XPS
BET surface area: 320 m^2/g

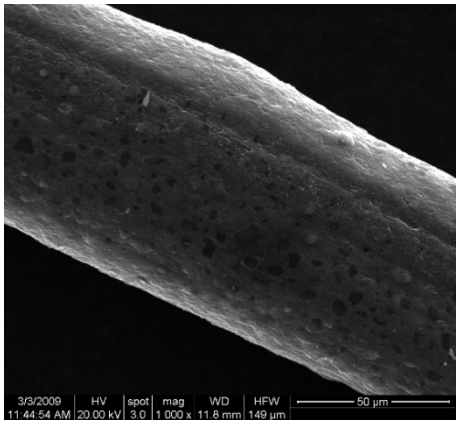
TEM elemental mapping; boron (red dots) is uniformly distributed

This provides a new synthetic route to boron substituted graphene scaffolds, and hence a new media for enhanced binding energy for H_2 uptake

Accomplishment: Spinning fiber, SWNT & graphene



Expanded SWNT fiber

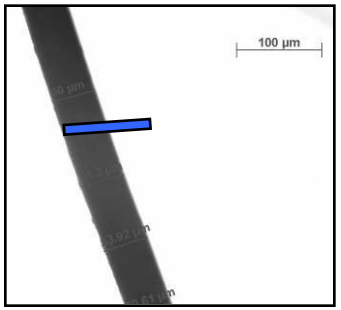


Graphene nanoribbon fiber

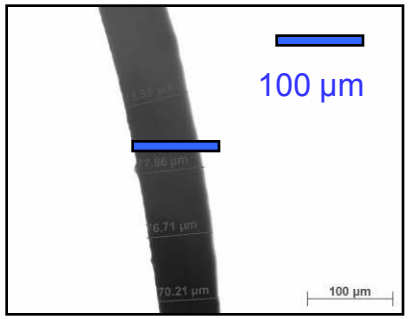
Graphene had not been made in significant amounts before 2006 [Noorden, Nature News, Vol 442 page 228]

Thermally conductive GNR can now be spun into a fiber just as for CNT

Represents earlier work, but sp^2 nanoengineered fibrous media is an ongoing goal.



Control = 52.83 µm
(Crosslinker omitted)



After crosslinking
= 77.5 µm

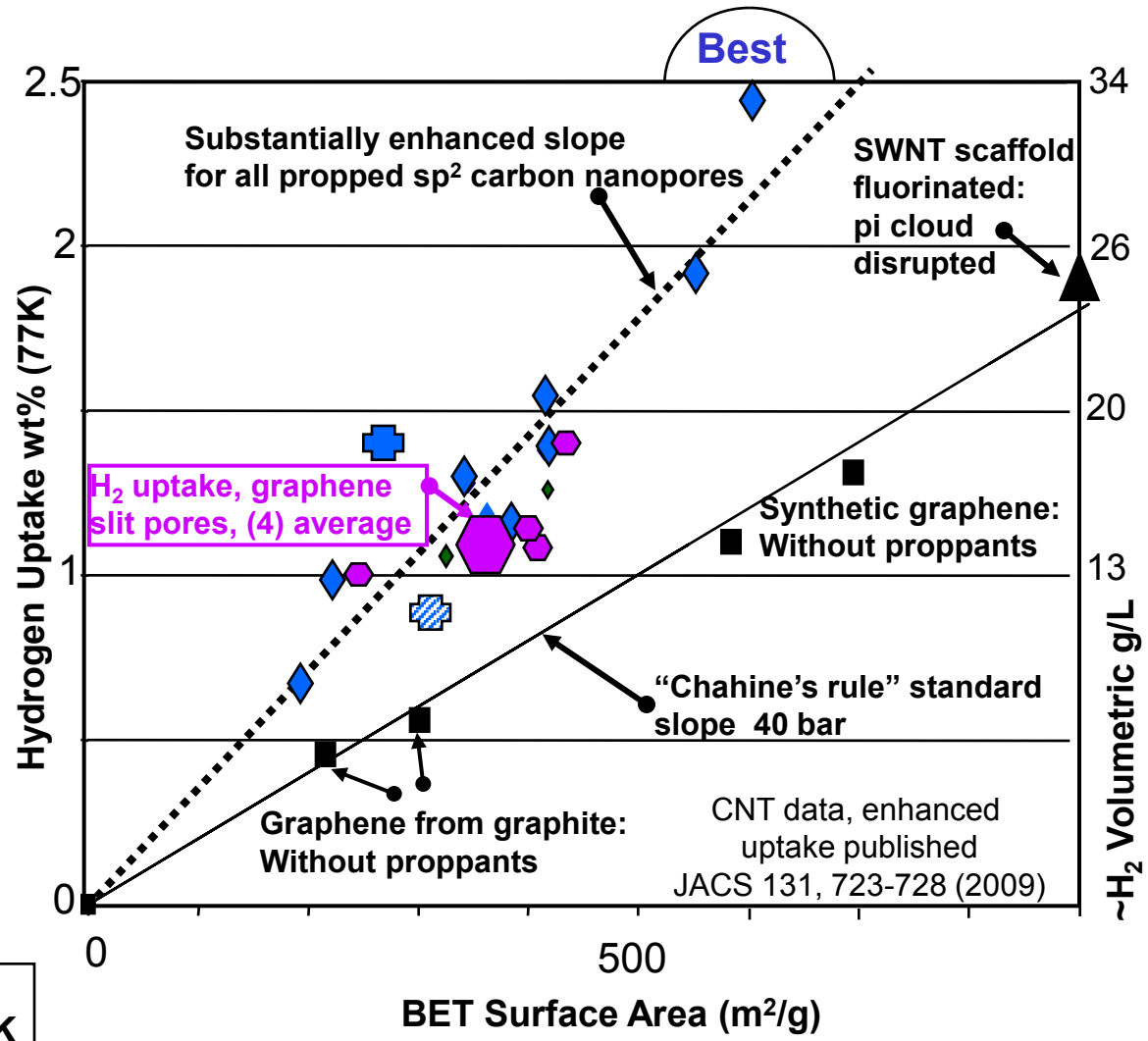
Crosslinking holds pores open, prevents collapse of graphene fiber when solvent is removed
[Graphene nanoribbons: Nature, 438, 872, (2009)]]

- **Fibers will have much better heat transport than powdered or granular media**
- **Less tortuousity for fast kinetics of uptake**
- **Industrial-type continuous spinning to produce media below 2015 DoE cost targets**

Accomplishment: Enhanced Uptake in sp^2 Propped Nanopores

Overall project accomplishments are summarized on the graph. Propped SWNT and graphene are on same plot. Includes disrupted pi cloud & without proppants.

- 1) Blue diamonds: SWNT scaffold expanded and cross-linked
- 2) Black triangle: F kills pi cloud
- 3) Large hexagon: average of 4 propped graphene measurement
- 4) Blue cross: (**new**) thermally expanded graphene sulfonate proppants. Li intercalated
- 5) Black squares: (**new**) synthetic graphene without proppants



Collaboration with NREL – all H_2 uptake measurements 2 bar, 77K

Design of engineered nanospaces using sp^2 material has shown unusually high H_2 uptake per unit surface area. Best uptake is 2.4wt% ≈30 g/L as the sp^2 carbon is a high density material. [Extrapolate best uptake to 40 bar: 35 to 40 g/L.]

Accomplishment: B,N,P Atom Substituted Graphene with H_2 Uptake

Making chemically synthesized atom substituted graphene; goal of 25% atom substitution

1. High nitrogen substitution has been achieved, range of 18% to 28%.
2. Good success achieved with phosphorous, which enhanced binding energy and high 17at% achieved (17at% not yet tested for H_2 uptake)
3. These atom substituted materials have not been propped open and in almost all cases show no enhanced uptake.

Binding energy:

sample	Atom	at%	kJ/mol
99D	B	5.4	8.6
99I	P	7.5	8.3
99L	N	18	5.6 (no enhancement)

Binding energy extrapolated to zero coverage. P shows 5.5 kJ at 1wt%.

No enhanced binding energy observed for nitrogen substitution, as theoretically predicted.

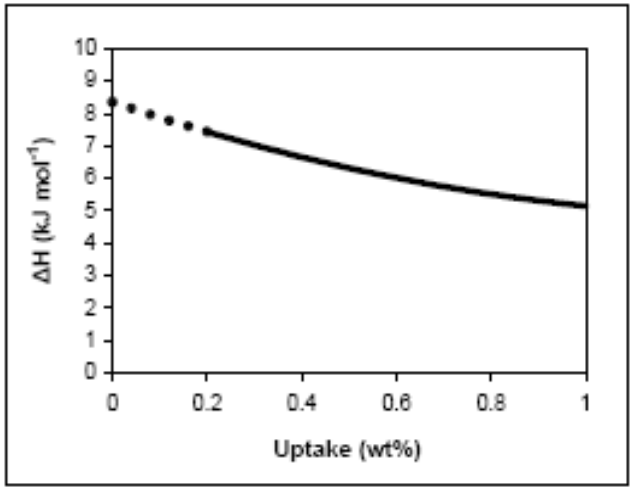
Many thanks to Channing Ahn of Caltech for these measurements.

Measurements made in collaboration with Channing Ahn at Caltech HSCoE partner
Concept of substituted nitrogen as binding site developed in collaboration with Air Products, industrial partner

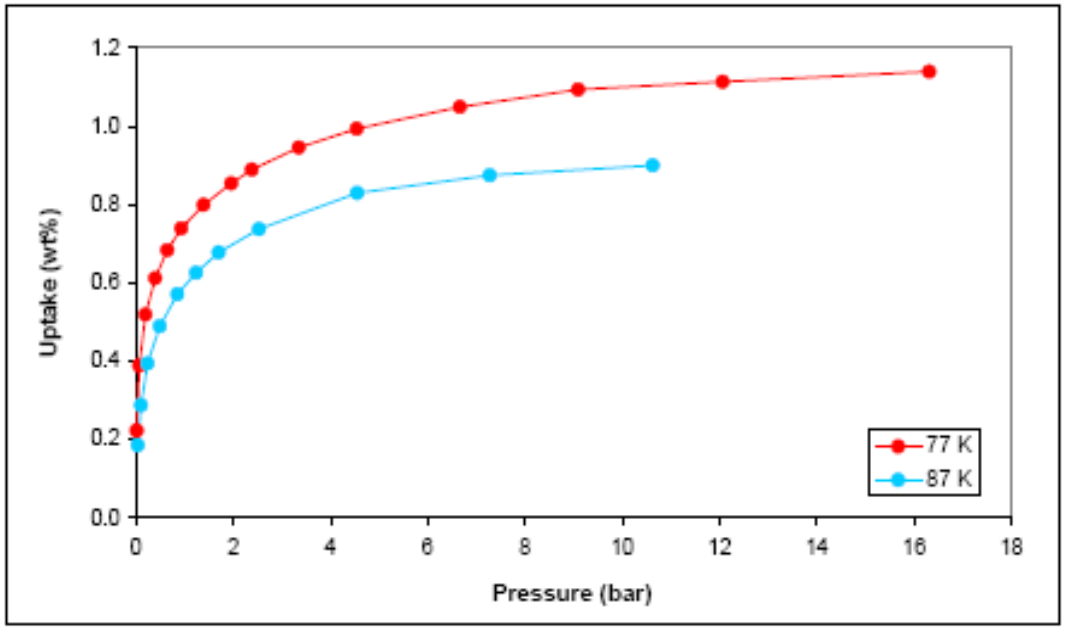
- **New liquid-based graphene synthesis is adaptable to atom substitution.**
- **Atom substitution directly increases binding energy**
- **Can provides attachment sites for species that increase binding energy**

Collaboration: Channing Ahn, Caltech isotherms P-substituted graphene

Isosteric Heat Analysis	
Extrapolated Adsorption Enthalpy at Zero Coverage (kJ mol^{-1}):	8.3

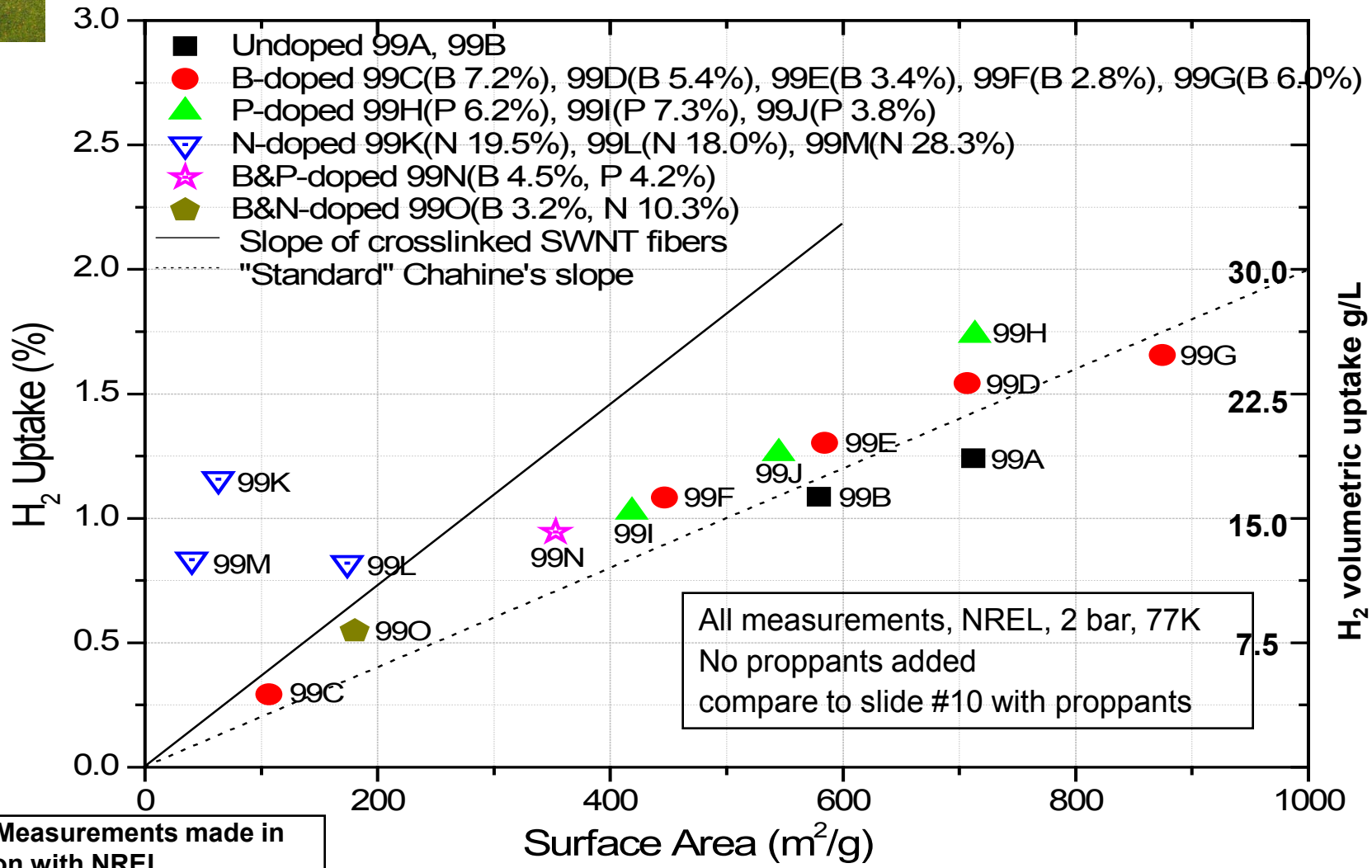


Isotherm Data			
77 K		87 K	
Pressure (bar)	Uptake (wt%)	Pressure (bar)	Uptake (wt%)
0.0	0.22	0.0	0.19
0.1	0.39	0.1	0.29
0.2	0.52	0.2	0.39
0.4	0.61	0.5	0.49
0.6	0.68	0.9	0.57
0.9	0.74	1.2	0.63
1.4	0.80	1.7	0.68
2.0	0.85	2.5	0.74
2.4	0.89	4.6	0.83
3.3	0.95	7.3	0.87
4.5	0.99	10.6	0.90
6.7	1.05	14.5	0.86
9.1	1.09		
12.1	1.11		
16.3	1.14		
22.9	1.13		



Phosphorous atom substitution into graphene behaves like boron in providing substantially increased H_2 binding energy, which will lead to higher temperature uptake

B,N,P Substituted Graphene – H_2 Uptake



Samples made by Zhong Jin

H_2 uptake Measurements made in collaboration with NREL

New versatile & scalable liquid-based synthesis of atom substituted graphene allows for a wide range of new H_2 adsorbent materials. Best H_2 uptake = 27 g/L, 2 bar pressure

Estimate best uptake at 40 bar: (10% to 30% increase) = 30 to 35 g/L

Accomplishment: Templated growth on SiO_2

Liquid-based synthesis of graphene allows for easy addition of silica nanoparticles for templated growth of atom-substituted graphene

Sample # and type of atom substitution	BET Surface area Degas 400 °C
ZJ-I-111A Boron	601.23 m^2/g
ZJ-I-111B Boron	374.84
ZJ-I-111C Phosphor	377.08
ZJ-I-111D Phosphor	392.13
ZJ-I-111E Nitrogen	318.46

X-Photoelectron spectroscopy analysis Atomic %

ZJ-I-111A	ZJ-I-111B	ZJ-I-111C	ZJ-I-111D	ZJ-I-111E
C1s 96.5	C1s 95.3	C1s 79.7	C1s 95.5	C1s 77.8
B1s 3.4	B1s 4.6	P2p 17.2	P2p 4.3	N1s 22.1
Cl2p 0.1	Cl2p 0.1	Cl2p 2.1	Cl2p 0.2	Cl2p 0.1

Planned H_2 uptake measurements to be made in collaboration with NREL

The successful of templated growth on silica nanoparticles opens up the option of using a wide variety of template materials. High atom% of phosphorous should provide enhanced binding energy for H_2, enhancement observed for 7.5at%, and now we have reached 17at%.

Project summary

Technical Accomplishments and Progress

Propped graphene nanopore scaffold showed similar enhanced uptake as SWNT nano-pore scaffolds; unpropped graphene showed an absence of enhanced H_2 uptake

Developed new liquid based method of chemical synthesis of graphene, measured H_2 uptake

Developed boron atom substitution in the graphene, then expanded atom substitution to include nitrogen and phosphorous

Extensive testing of H_2 uptake; density ~1.5 g/cm^3, gives better volumetric capacity

Enhanced binding energy observed for boron and phosphorous atom substitution, but not for nitrogen

Developed silica nanoparticle templates for synthesis of atom-substituted graphene

First test with new P-substituted graphene, (6.2at%) just 2 bar test pressure, H_2 uptake very close to DoE volumetric goal of 28g/L (**materials only)

Achieved high phosphor substitution of 17at% (not yet tested for H_2 uptake)

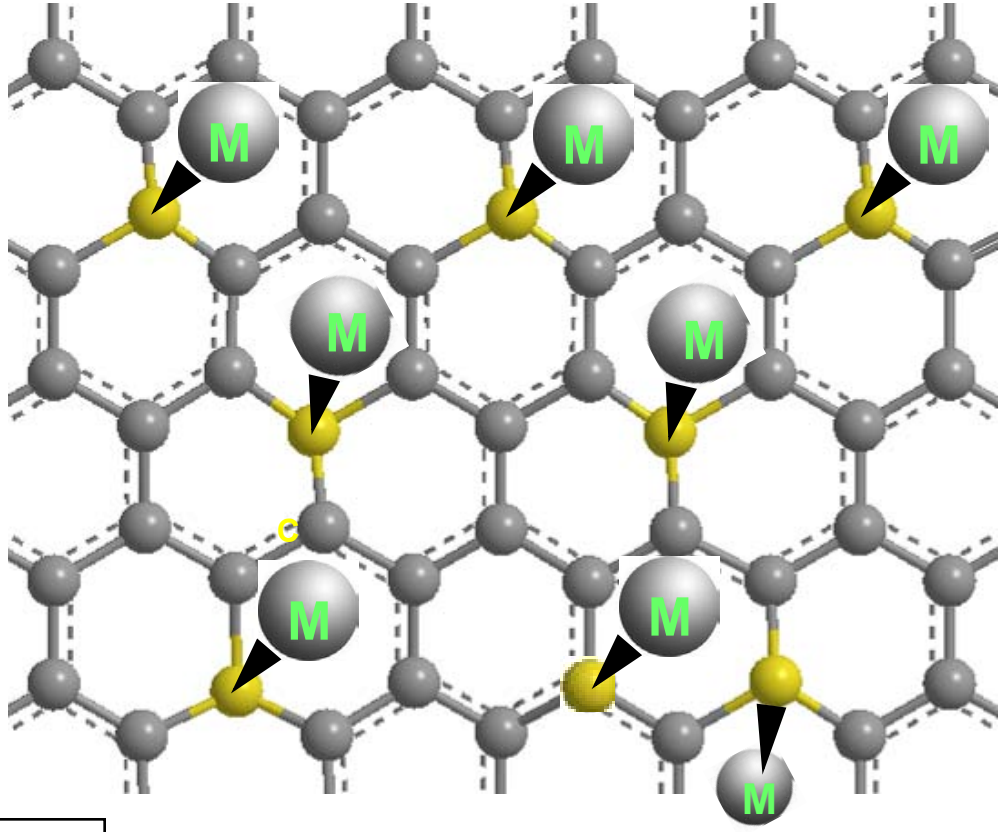
All experiments are directed toward creation of low cost nanoengineered graphene scaffolds with for fully reversible uptake of hydrogen with goal of >4.5wt% and >50 g/L. Addition of charged species will shift uptake close to RT.

Future direction: Graphene with metal functionalization on substituted nitrogen

Our success with high % of atom substitution (up to 25%) indicates that we can bind individual metal atoms on the graphene scaffold & overcome previous problem of low density of “parking spots”.

Nitrogen readily forms a complexes with many metals. The density of atoms on the graphene surface will depend on the % atom substitution.

Such complexes should stabilize many moieties, even metals that tend to cluster such as titanium. Charge transfer is likely in most cases, and such will enhance H_2 binding to the graphene.



Carbon

N or P substitution

M Metal atom above (or below) graphene plane

Collaboration:
Our Oak Ridge NL partners calculated 8wt% H_2 uptake on calcium-coated C60. We propose here the flat version i.e., graphene in a scaffold.
[Yoon et al,. PRL 100, 206806, (2008)

This provides a new route to metal functionalized graphene scaffolds, and hence a new media with sufficient H_2 binding energy for RT uptake.

Future work

FY-10

- Test H_2 uptake on the new silica nanoparticle templated graphene
- Test H_2 uptake and binding energy on high % P-substituted graphene
- Develop proppants for atom-substituted graphene for enhanced uptake.
- Consider the exceptionally high N- and P- substituted graphene to provide abundant stable binding sites for metal atoms.

We believe that our approach provides this unique combination: sp^2 nanopores that provide enhanced uptake per unit SA, a high density media, and now the option of metal atom functionalization on a large number of sites.
These features will converge to make a media that exceeds DoE 2015 volumetric goals, and at temperatures much closer to RT.

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)					
Storage Parameter	**Units**	**2010 System Target**	**FY08 nanoengineered graphene & alternating layered metal****	**FY09 nanoengineered graphene***	**FY10 atom-substituted graphene****
Specific Energy	kWh/kg (wt% H2)	**1.5 (4.5 wt.%)**	**Calculated 3.5** kWh/kg **10.9wt% 9.5wt% excess**	**0.8** kWh/kg **2.4wt% CNT 1.4wt% G**	**0.6** kWh/kg **1.8wt% G**
Volumetric Energy Capacity)	kWh/L g/L	**0.9 28g/L**	**Calculated 2.7** kWh/L **81g/L 71g/L excess**	**1.0** kWh/L **30 g/L CNT 18.2 g/L G**	**0.9 to 1.1*** kWh/L **27g/L to 35*g/L Graphene**
Desorption T			Calculated≥ 253°K	>77°K	>77°K
Plateau Pressure			100 bar fill pressure	Measured at 2 bar	Measured at 2 bar; *est 40 bar

- **Graphene nanoengineered media has undergone rapid development this year**
- **Atom substituted graphene provides enhanced binding energy and sites for metal atom attachment that can bind H_2 at near ambient temperatures**

Notes:

FY08 For metal doped graphene scaffold; calculated volumetric for 100 bar fill pressure (delivered)

FY09 Transition from carbon nanotube (CNT) to the development of spun fiber graphene media

FY10 Proppants are not yet developed for atom-substituted graphene, & enhanced uptake is not observed.