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

Nanoengineered Graphene Scaffolds with Alternating Metal-Carbon Layers for H_2 Uptake at Ambient Temperatures

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Project ID #ST_30_Kittrell

(Cloning Single Wall Carbon Nanotubes for Hydrogen Storage)

Overview

Timeline

- Start-Feb 2005
- Finish-Jan 2010
- 80% complete

Budget

- Total project funding
- DOE share $1,765,989
- Contractor share $441,497
- Funding for FY07- $300,000
- Funding for FY08- $400,000
- Funding for FY09- $350,000

Barriers

- General
  A. Cost.
  B. Weight and Volume
  C. Efficiency
- E. Refueling Time
  Reversible Solid-State Material
  M. Hydrogen Capacity and Reversibility
  N. Lack of Understanding of H Physi- and Chemisorption

Partners

NREL, Oak Ridge National Lab
Air Products, Caltech, Penn State,
Duke, Yakobson/Hauge at Rice

DOE 2010 Targets for Storage System
- Gravimetric 60 g H_2/kg
- Volumetric 45 g H_2/L

Objectives

The primary objective is to design and produce nanoengineered carbon-metal media and/or mobile nanoparticle catalyst in a graphene slit-pore scaffold to achieve:

1) >9wt% uptake of hydrogen

2) >80 g/L at near-ambient temperatures.

And simultaneously meet all major DoE 2015 targets, and other desirable traits:

3) **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)

4) **High energy efficiency**: Lowest possible ΔS, hence lowest –ΔH for <10% energy loss, less heat with fill.

5) **Unrestricted kinetics**: Little or no activation barrier for adsorption, engineered H_2 gas channels in fiber

6) **Thousand fill cycles**: No material fatigue using rigid slit pores. 1/10,000 water wt/wt H_2 → 10% capacity loss for ~400,000 mile lifetime range.

7) **Near-ambient temperature**: Alternating layer donor-acceptor complex is a H_2 nano-compressor at RT

8) **Cost target of \$67/kg H_2:** Low cost graphite and sodium; common industrial fiber spinning process.

9) **Media density ~1g/cc**: Volumetric and gravimetric capacities track well; targets are not in conflict.

10) **Avoid extreme temperature swings**: Dynamic multilayer adsorption (DMLA) means that all adsorbed H_2 are equivalent, yielding the smallest temperature change with >90% delivery.

11) **Understand all forces of attraction** that make this hydrogen nano-compressor operate.

This will be accomplished with:

Fibers spun from a graphene slit-pore nanoengineered scaffold:

With **alternating layers of carbon and metal atoms on "parking spots"**: The charge transfer complex generates pore filling dipole-induced-dipole attraction for dynamic multi-layer adsorption ~RT

Or with **mobile catalyst particles** to convert graphene to hydrogen-saturated graphane.

Milestones 2008-09

Month/Year	Milestone
Sept-08	Develop “parking spot” for alkali metal & with hydrogen uptake near ambient temp. for graphene and CNT (pyridine functionalized CNT fiber successful)
Nov-08	Add capability of making low cost cross-linked graphene scaffolds (done)
Dec-08	Develop crosslinkers for graphene, test for hydrogen uptake in graphene engineered nanospaces, look for same enhancement as for CNT scaffolds (done)
Feb-09	Develop metal atom intercalation and in-situ diagnostic to prove successful charge transfer doping (done) No-go for titanium and scandium intercalation
May-09	Develop spinning process to make graphene fibrous media similar to CNT fiber (demonstrated)
Aug-09	Add “parking spots” for immobilized alkali metal atoms by making pyridine-functionalized graphene and measure hydrogen uptake/release at first sample made near-ambient temperature (functionalization demonstrated)
Dec-09	Demonstrate that the metal intercalated slit-pores of the graphene media will have a volumetric uptake of 45 g/L for near-ambient temperatures.
Dec-09	Create mobile Pd metal nanoparticle catalyst in graphene scaffold for direct catalytic hydrogenation/dehydrogenation near ambient temperature (first experiment done)

Approach: Making the nanoengineered 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

All the methods necessary to create the metal-intercalated graphene scaffold and transfer the expertise developed for carbon nanotube (CNT) scaffolds are being developed and tested to create the low-cost hydrogen uptake media.

Develop and exploit sources of graphene and graphene nanoribbons a new low cost slit-pore nanoporous media

Prop open graphene sheets to make engineered nanospaces, by transferring expertise in functionalization and crosslinking of CNT

Intercalate nanoscale Pd catalyst particles into graphene for dissociative chemisorption

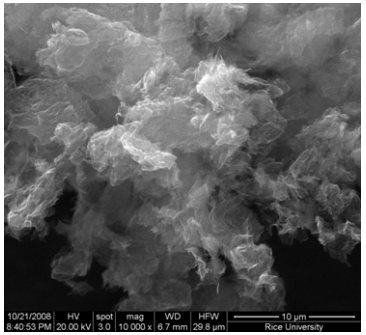
Develop fiber spinning methods for graphene to make fibrous media

Verify the ~2x enhancement in hydrogen uptake vs. “Chahine’s rule” for nanoporous sp^2 carbon

Develop alkali metal intercalation and diagnostics to show charge transfer, and measure hydrogen uptake

Demonstrate dipole-induced-dipole binding for hydrogen will lead to dynamic multi-layer adsorption for the highest possible uptake per unit surface area for near-ambient temperatures.

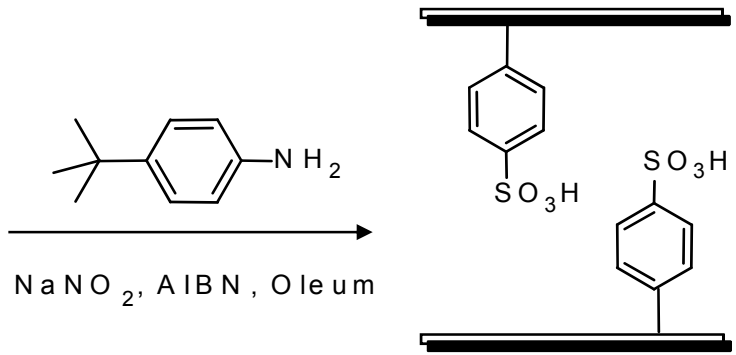
Accomplishment: Propping Open Graphene Scaffold



Exfoliated graphene:
short SWNT for proppant
75:25 ratio

+

Short
CNT



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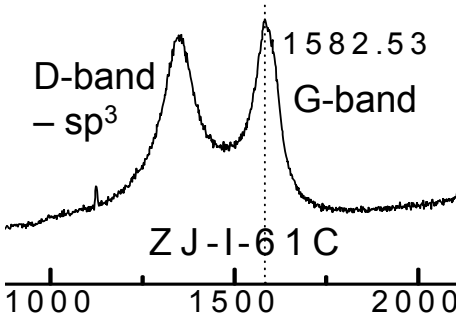
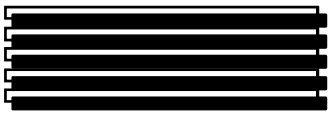


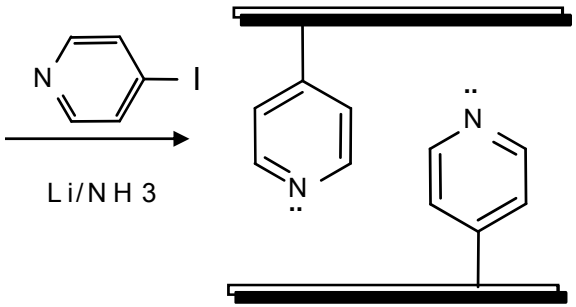
Good Raman spectra

SWNT proppant + functional groups →
Graphene scaffold with much improved SA = 1005 m²/g

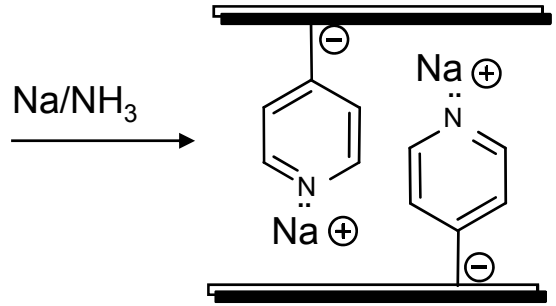
[Publication Functionalization of graphene sheets; Tour 2008]



Exfoliated graphene



Accomplished



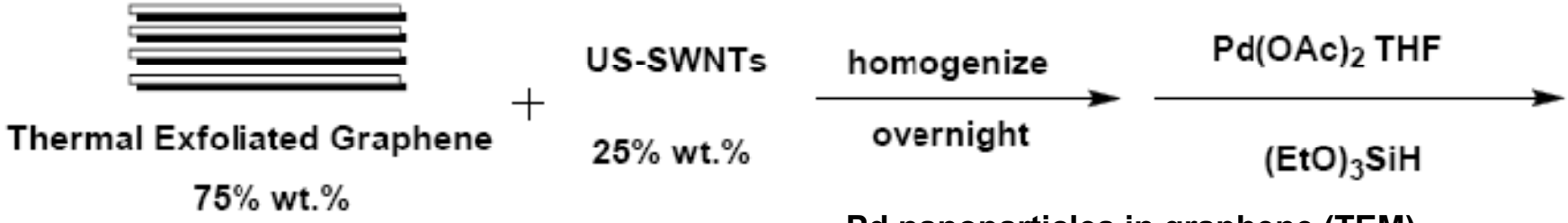
Next step

Pyridine functionalization to make alkali atom "parking spot", showing alternate lithium/ammonia functionalization

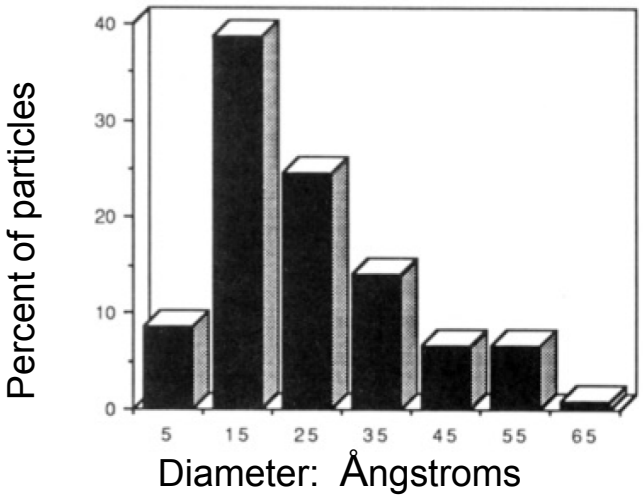
Subsequent sodium intercalation

Technology transfer: Successful chemistry with SWNTs being transferred to graphene.
"Parking spot" for metal atom on graphene: Enhanced binding for H_2 uptake ~RT.

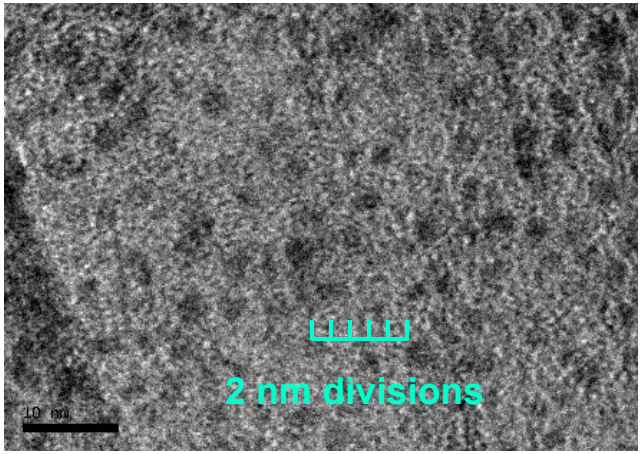
Accomplishment: Pd catalyst intercalation of graphene



Previous work: Size distribution of Pd particles on xerogel [ref. Tour 1990]



Pd nanoparticles in graphene (TEM)
range 1.5 to 3 nm dia. Pd about 5wt%; scale bar 10 nm.

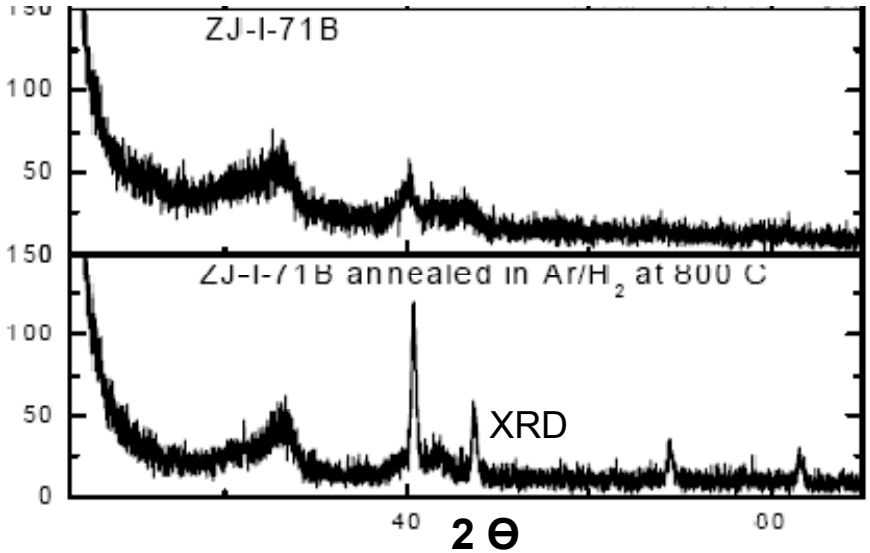


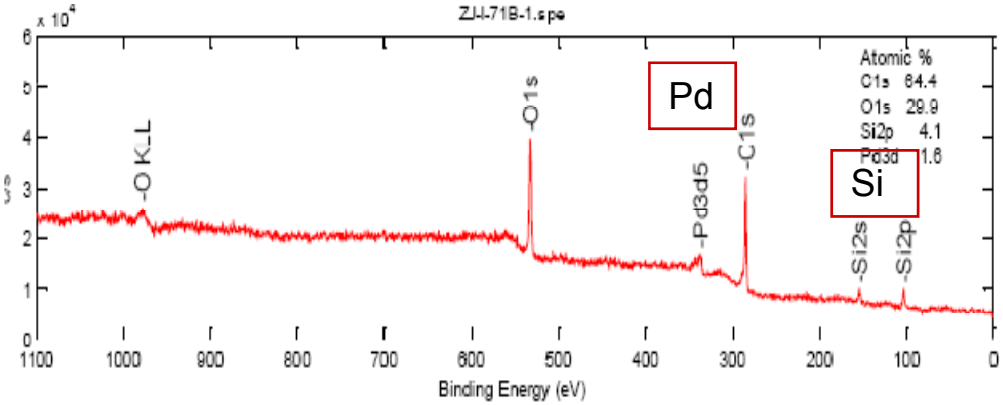
The key to direct catalytic deposition of hydrogen is to generate catalyst particles sufficiently small to be mobile in the nanospaces of the graphene scaffold. The previous work yielded many particles 1.5 nm diameter.

Insight from HSCoE: Our APCI partners have calculated that hydrogen binding to graphene with catalytic Pt particles has both low ΔH and a low activation barrier.

Catalytic hydrogenation with mobile nano-catalyst particles can access all surface area in a graphene scaffold. Fully hydrogenated graphene will exceed 2010 weight & volume goals

Accomplishment: Pd catalyst intercalation of graphene





X-ray diffraction before and after shows formation of the nano-crystalline Pd catalyst particle at 40°

X-ray photoelectron spectroscopy reveals small amounts of silicon proppant along with the palladium.

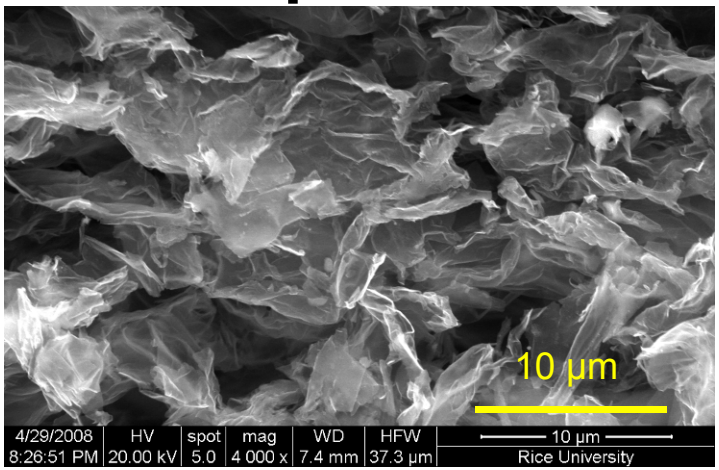
Samples sent to Channing Ahn at Caltech for testing. The ΔH for simultaneous formation of several covalent C-H bonds from H_2 is nearly thermoneutral. [Yakobson, AMR2008 presentation]; however, the activation barrier is very high, hence the mobile catalyst is needed to bond/release the hydrogen to the graphene surface

Reference: Example of mobile catalyst particles: cut single sheet graphene at much higher temperatures [Yakobson2008]

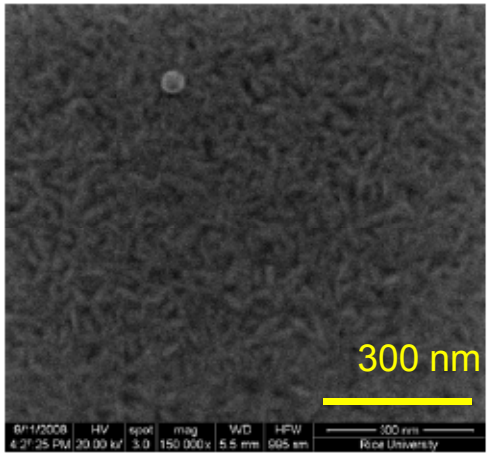
Scale-up now successful, plan to send graphene slit-pore samples to NIST to characterize by neutron scattering.

XRD and XPS diagnostics show successful uptake of the Pd catalyst and reduction to nanocrystals that can foster uptake/release of hydrogen at near-ambient temperatures

Accomplishment: Graphene – making the new media

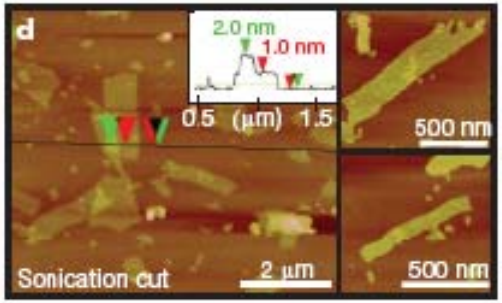


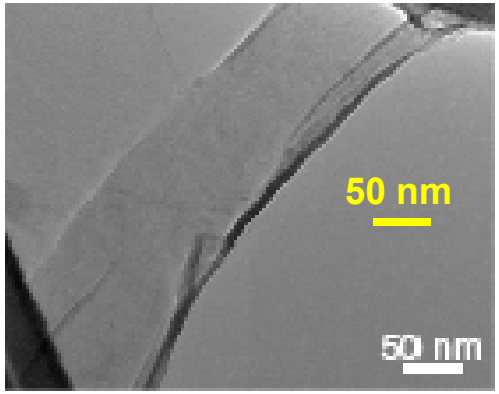
Natural and synthetic graphene: 3 methods



Graphite + sulfuric acid + oxidizer = graphene

Graphene grown by chemical vapor deposition





AFM, SEM and TEM images of single sheet Graphene nanoribbons

Graphene by chemical unzipping multiwall carbon nanotubes (MWCNT). The above images all show graphene as single layers, essential for maximum surface area. [Tour 2009a]

The MWCNT source material is now being produced by the ton as a durability enhancer in Li+ battery electrodes.

- **Graphene obtained from mineral graphite and simple acid processing**
- **Graphene grown synthetically from carbon-containing feedstock**
- **Source material for H_2 storage media well below 2015 costs targets**

Accomplishment: Enhanced H_2 uptake also for graphene

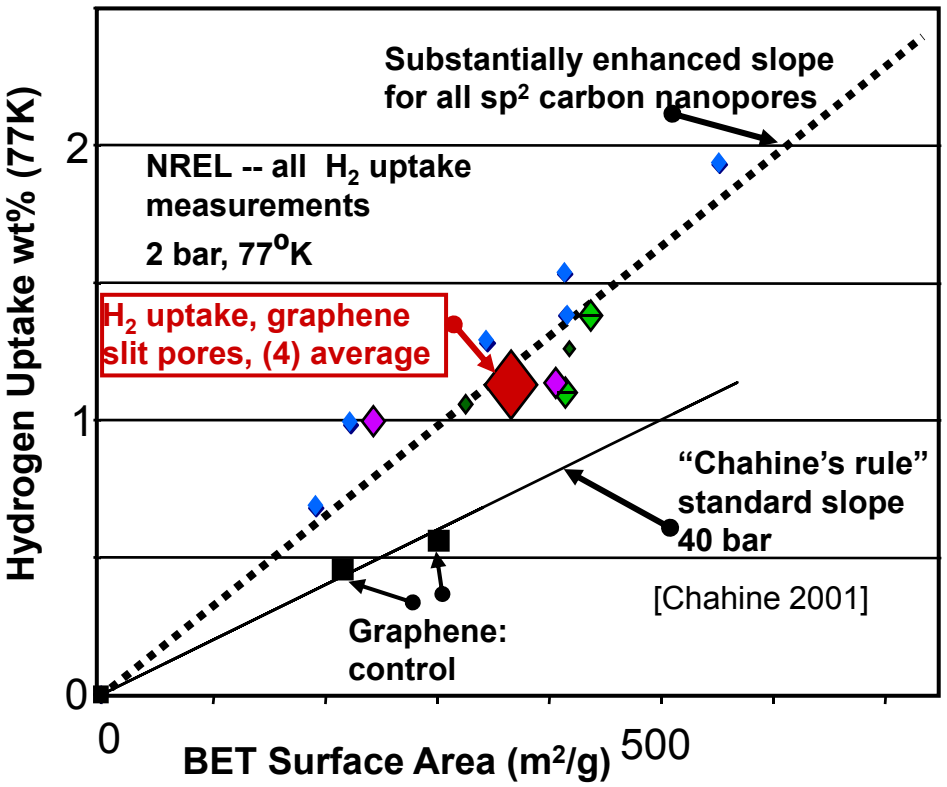
Enhancement of H_2 uptake in new graphene slit pores vs. CNT enhancement. Average of 4 tests.
Two samples two tests each, H_2 uptake after bakeout 500ºC & 700ºC

Graphene & oleum expansion
Grinding with dipheynl- & chlorophenyl- aniline

Graphene & oleum expansion
Stirring with t-butyl-aniline

Graphene, ionic liquids: Control
Crosslinking without oleum expansion
= no enhanced uptake
Grinding with dipheynl- & chlorophenyl- aniline

CNT Oleum expansion and crosslink
Smaller diamond symbols provide reference points for CNT comparison with new graphene work.
Publication: 1.85x steeper slope vs. Chahine's rule [Tour 2009b]:

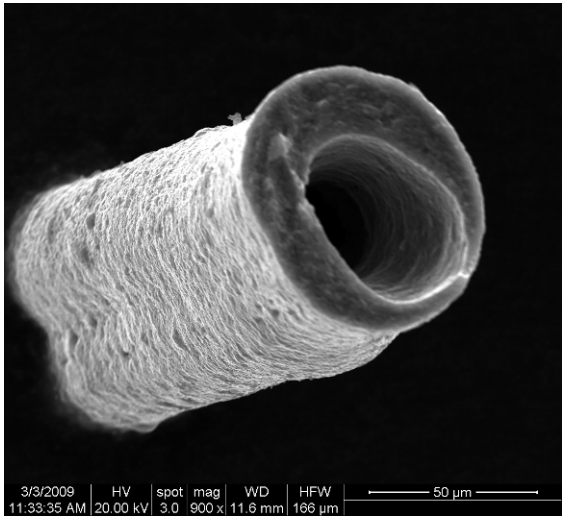


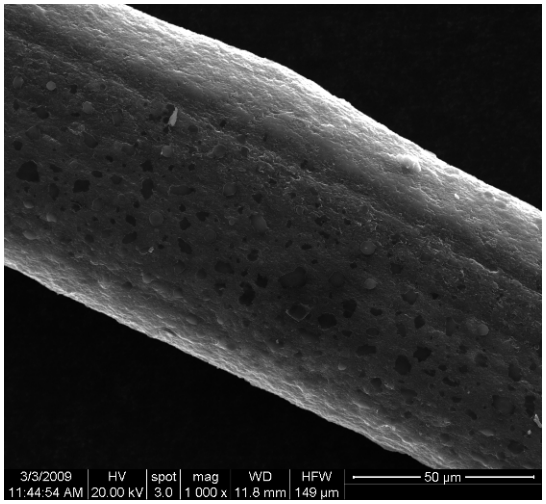
Bakeout ≥300C needed to remove solvent from slit pores

Graphene enhancement: theory [Patchkovskii 2005]
Supercritical H_2 uptake sp^2 carbon, experiment, [Iijima 2002]

- **Graphene scaffold, like CNT also >1g/cc: H_2 volumetric enhancement tracks gravimetric**
- **The hydrogen nano-compressor: Nanoengineered graphene slit pores also pull in H_2:**
- **Highly enhanced H_2 uptake per unit SA is an alternate route to reach 2015 targets**

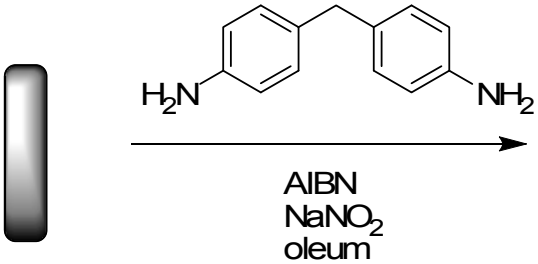
Accomplishment: Spinning fibers from graphene





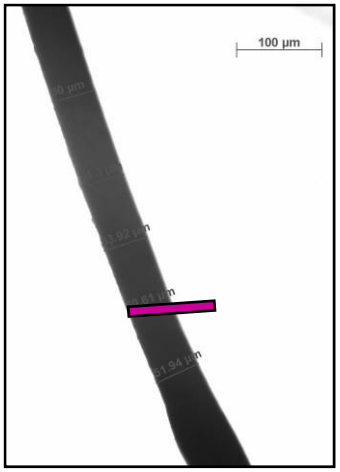
Graphene is "the new kid on the block" and had not been made in significant amounts before 2006 [Noorden 2006]

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

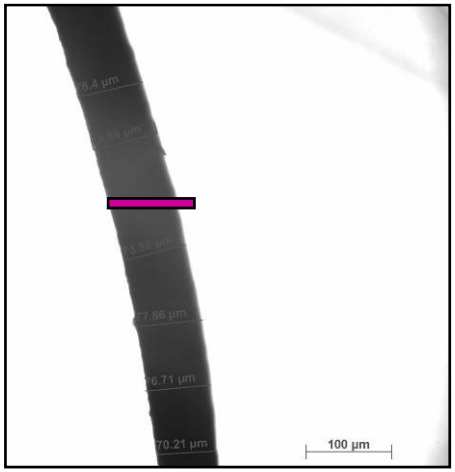


Graphene nanoribbons spun into fibers and crosslinked
[Graphene nanoribbons publication: Tour 2009a]

Scale bar is 100 µm



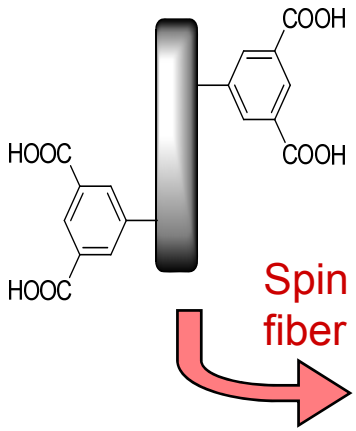
Control = 52.83 µm
(Crosslinker omitted)

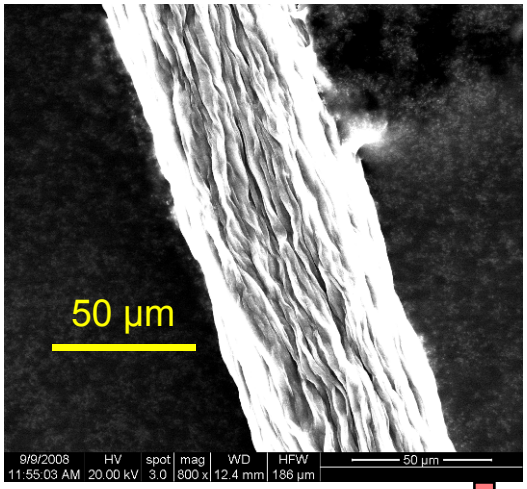


After crosslinking
= 77.5 µm

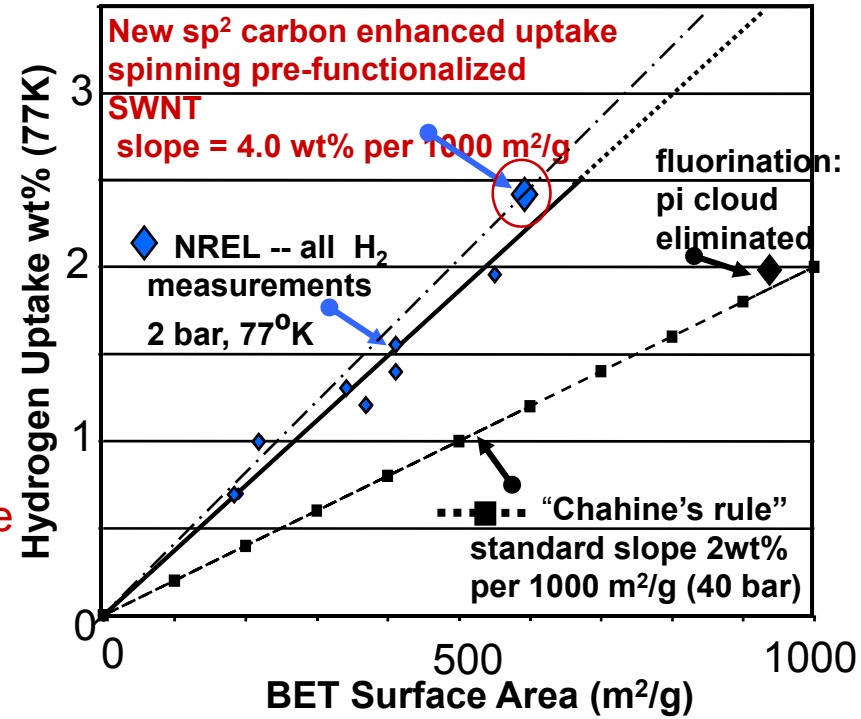
- **Conductive fibers will have much better heat transport than powdered or granular media.**
- **Industrial-type continuous spinning to produce media, below 2015 DoE cost targets**
- **Unlimited cycling does not degrade rigid nanoengineered scaffold**

Accomplishment: Enhanced Uptake sp^2 Nanopores





H_2 Uptake



Nanotubes are pre-functionalized with isophthalic acid for more uniform separation
Best uptake yet!

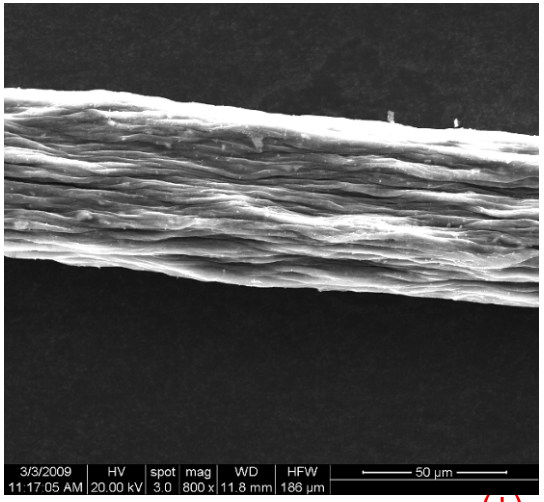
Crucial test demonstrate that H_2 enhanced uptake per unit surface area is retained for functionalized material, confirming that it is due to the engineered nanopore.

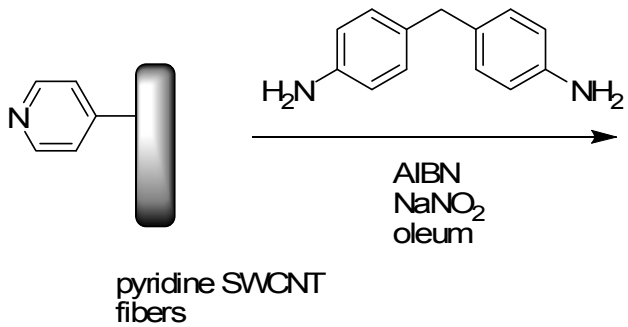
We have also demonstrated isophthalic acid attaches to graphene and will transfer this technology to make pre-functionalized graphene fibers

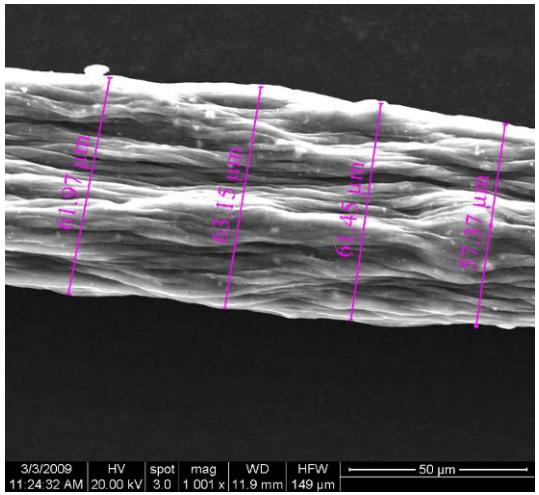
Smaller diamonds: Earlier published data 1.85x steeper slope vs. Chahine's rule [publ. Tour 2008]
ORNL partners also observe similar benefit of "ideal" pore size for sp^2 carbon nanohorns [AMR2008]

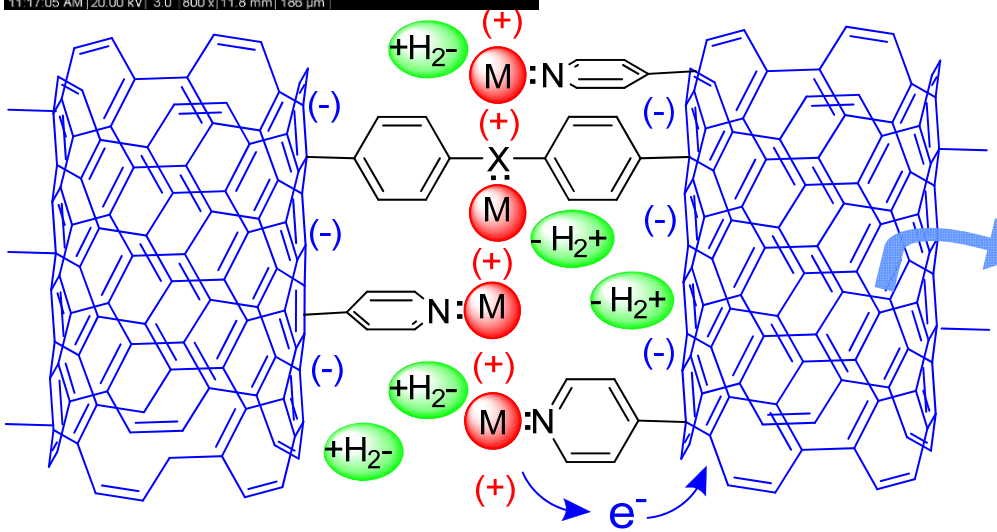
- **Pre-functionalized spinning dope streamlines the chemistry, greater H_2 enhancement**
- **Thermally conductive media reduces weight and cost of intra-tank thermal management**
- **Engineered macroporosity in woven fabric (or cables) for H_2 fill rates to meet 2015 target**

Accomplishment: Pyridine functionalization for metal anchor









Goal: Combine nanoengineered scaffold and "parking spot" for metal atoms

X = N or O

Alternating **(+)** and **(-)** layered nanopore

M = sodium metal (+)

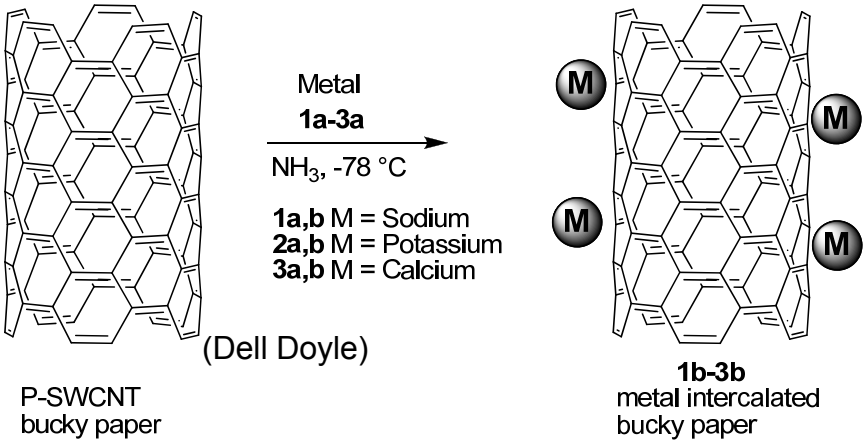
e^- = charge transfer to sp^2 carbon

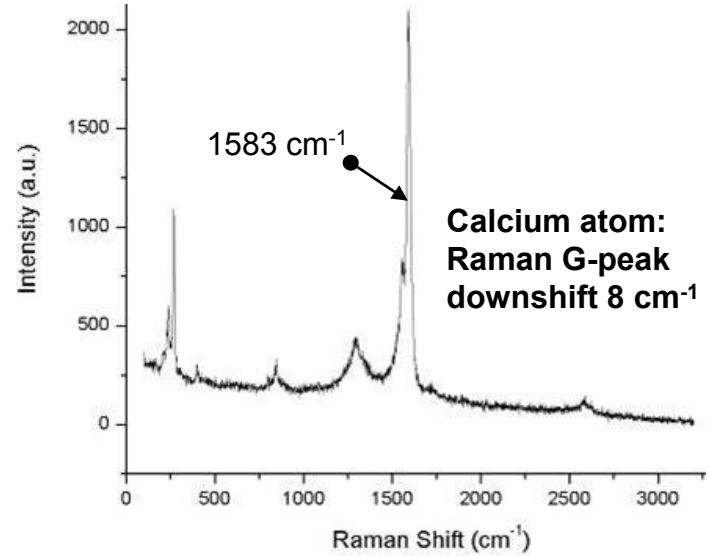
– H_2+ = polarized H_2 enhanced binding

Sodium metal addition now underway to make nanoengineeered donor-acceptor complex
Charge transfer adds dipole-induced-dipole forces for stronger attraction of H2

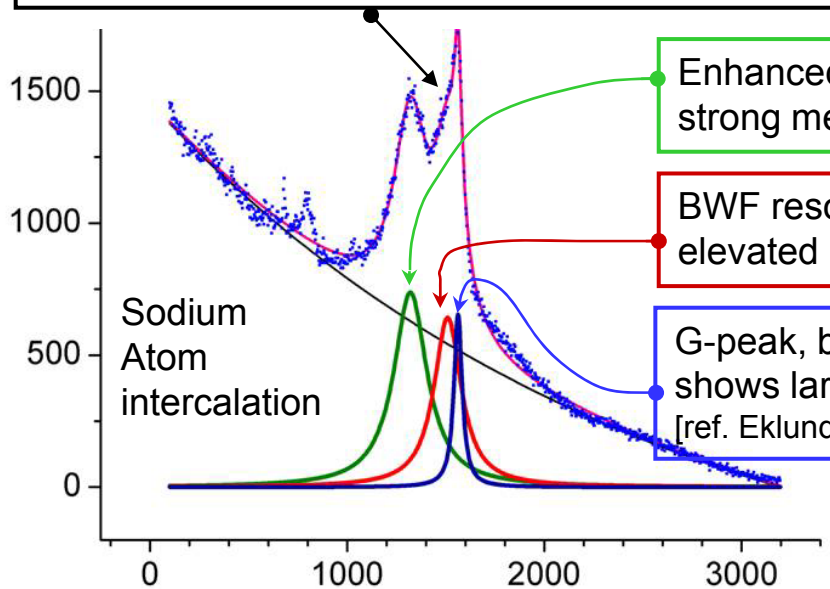
- **The hydrogen nano-compressor packs the pores at near-ambient temperatures**
- **No activation barrier for fastest fill kinetics and low ΔS for maximum energy efficiency**

Accomplishment: Donor-Acceptor Complex & Diagnostic





Sodium DAC: Complex band structure develops
Deconvolution into 3 bands, excellent fit to **Spectral data**



Enhanced D-band 1321x cm^{-1}, strong metal-atom sidewall interaction

BWF resonance 1510 cm^{-1}, elevated Fermi level, electrons added

G-peak, big Eklund downshift 1563 cm^{-1}, shows large charge transfer Na to SWNT [ref. Eklund 2002]

Sodium atom on CNT: big Charge Transfer to sp^2 carbon; potassium also works well.

Calcium: only modest CT observed

Ca efforts spawned due to theory work by ORNL partner [Yoon 2008]

[DAC observed to give metallic character to semiconductor materials: Morpurgo 2008]

- **Raman diagnosic developed for in situ monitoring of CT due to intercalating atom in scaffold**
- **Intercalation critical step for nanopores with dipole-induced-dipole forces to nano-compress H_2 @RT**

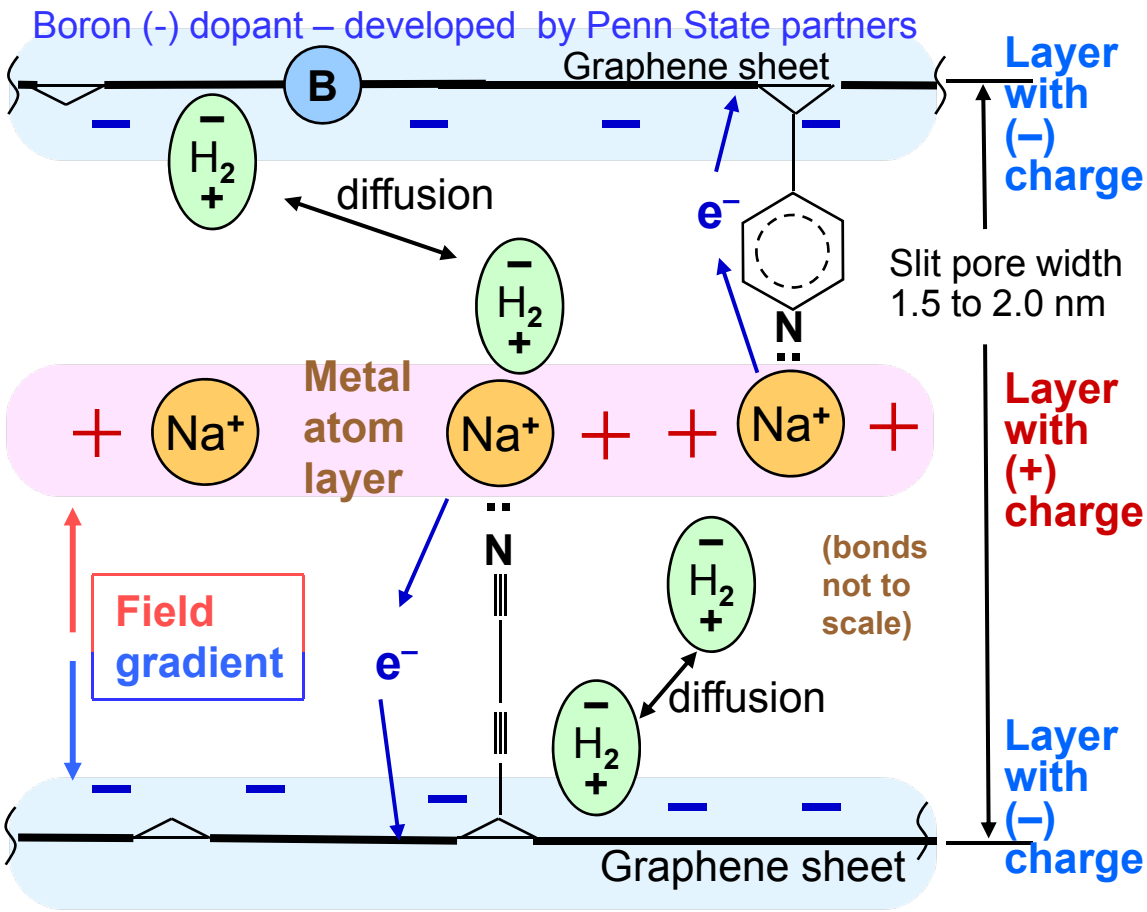
Accomplishment: Concept of dynamic multilayer adsorption

2003 DoE BES Workshop on H_2 [BES 2003], **multilayer H_2 adsorption was considered necessary**

Problem: A second layer of hydrogen will invariably be weakly bound, wide temperature swings needed.

Solution: Alternating layers of charge with metal atom electron donors and graphene acceptors.

Covalently bonded metal atom held in place with M-C, M-N, or M-O bond, prevents aggregation.



The donor-acceptor complex creates a permanent electrostatic dipole that permeates the nanopore which polarizes the H_2.

Root of the concept from ORNL partners. Mina Yoon calculated 1.2 eV attraction for 6 H_2 (0.2 eV each H_2) in the separated DAC TTF/TCNQ, & H_2 on C_{60}+ [Yoon 2007, 2009}

The hydrogen randomly diffuses in the pore, all H_2 experiences the same dipole-induced-dipole potential throughout.

This is the equivalent of a multilayer adsorption, but it is dynamic, not static.

- **New type of alternating charge slit pore of adds dipole-induced-dipole potential and DMLA.**
- **$-\Delta F = RT\ln K \sim 13$ kJ/mol, adequate to packs the pores with H_2, with K = 35 (corrected for fugacity)**
- **Fill pressure 100 bar; density equivalent ~3500 bar in the pore**

Project summary

Technical Accomplishments and Progress

Developed several sources of graphene and graphene nanoribbons a new low cost nanoporous media

Developed methods to open and crosslink graphene sheets to make engineered nanospaces, similar to previous work with CNT

Began work on the mobile Pd catalyst on graphene for uptake/removal of hydrogen near ambient temp.

Developed fiber spinning methods for graphene to make fibrous media

Apply expansion and crosslinking developed for CNT to graphene fibers

Continued with experiments to verify the sp^2 carbon nanopore enhancement in hydrogen uptake vs. “Chahine’s rule”, now for nanoengineered graphene and pre-functionalized CNT

Show how to expand enhanced uptake to a concept of dynamic multi-layer adsorption for hydrogen uptake near-ambient temperatures using a donor-acceptor complex from layers of metal atoms and graphene.

All experiments are directed toward creation of nanoengineered scaffolds with intercalated catalyst or layered metal for reversible uptake of hydrogen at near-ambient temperatures, with goal of >9wt% and >80 g/L.

Future work

FY09-10

- Continue to develop graphene expansion and crosslinking methods → transfer top notch expertise in SWNT sidewall chemistry to (new) single sheet graphene.
- Develop Pd mobile catalyst for direct hydrogenation/dehydrogenation at near-ambient temperatures
- Determine effective pore size for optimum Pd mobility, take into account kinetics of uptake and release, and optimizing volumetrics.
- Transfer the enhanced hydrogen uptake concept already proven for the the CNT scaffold to the alternating layer metal-graphene scaffold near RT; Determine added slit pore binding energy of dipole-induced-dipole potential
- Scale up the production of graphene slit-pore fiber (now underway); share with HSCoE partners for higher pressure H_2 uptake testing
- Obtain 45 g/L deliverable H_2 uptake at near-ambient temperatures

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)					
Storage Parameter	**Units**	**2010 System Target**	**FY07 nanoengineer fiber****	**FY08 nanoengineered graphene & alternating layered metal****	**FY09 nanoengineered graphene****
Specific Energy	kWh/kg (wt% H2)	**2.0 (6 wt.%)**	**0.67 2.0wt%**	**Calculated 3.5 kWh/kg 10.9wt% 9.5wt% excess**	**0.8 1.4wt% G 2.4wt% CNT**
Volumetric Energy Capacity)	kWh/L g/L	**1.5**	**0.67**	**Calculated 2.7 kWh/L 81g/L 71g/L excess**	**Density = 1.3 18.2 g/L G 30 g/L CNT**
Desorption Temperature			>77°K	Calculated ≥ 253°K	>77°K
Plateau Pressure			Measured at 2 bar	100 bar fill pressure	Measured at 2 bar

Notes:

FY07 Dihydrogen uptake as measured at 2 bar, not extrapolated to 30 bar

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

FY09 Transition from CNT to the development of spun fiber graphene media

G = graphene slit pore scaffold; CNT = carbon nanotube scaffold

- **Graphene nanoengineered media has undergone rapid development this year**
- **Made possible by drawing on similar expertise with CNT**

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Glossary

AIBN	**2,2-azobis(2-methylpropionitrile) a free radical initiator**
AFM	**atomic force microscopy**
BES	**Basic Energy Sciences**
BWF	**Brett-Wigner-Fano = phonon-electronic state resonance condition, occurs for "metallic" character**
CNT	**carbon nanotube**
CT	**charge transfer**
DAC	**donor-acceptor-complex**
DMLA	**dynamic multi-layer adsorption**
D-band	**Raman "disorder" mode characteristic of sp^3 sites or "defects" on sp^2 graphene carbon**
G-band	**Raman tangential mode characteristic of sp^2 graphene-type carbon, typically 1590 cm^{-1} shift**
G	**graphene**
GNR	**graphene nano-ribbons**
GO	**graphene oxide**
MWCNT	**multi-wall carbon nanotubes**
ORNL	**Oak Ridge National Laboratory**
Pd	**palladium**
Pt	**platinum**
RT	**room temperature**
SEM	**scanning electron microscopy**
SWNT	**single wall carbon nanotube**
TEM	**transmission electron microscopy**
TTF	**tetrathiofulvalene – electron donor and the**
TTNQ	**tetracyano-p-quinodimethane -- electron acceptor**
XPS	**X-ray photoelectron spectroscopy**