Nanoengineering the Forces of Attraction in a Metal-Carbon Array for H_2 Uptake at Ambient Temperatures

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Poster Session

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Project ID
#STP12

(Cloning Single Wall Carbon Nanotubes for Hydrogen Storage)

Overview

Timeline

- Start-Feb 2005
- Finish-Jan 2010
- 60% complete

Budget

- Total project funding
- DOE share $1,715,990
- Contractor share$428,997
- Funding for FY05-$300,000 plus $82,000 cost share
- Funding for FY06-$300,000 plus $82,800 cost share
- Funding for FY07- $300,000 plus
- $85,697 cost share
- Funding for FY08- $400,000 plus
- $88,697 cost share

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, C. Ahn at Caltech
Duke, Penn State and
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 layered carbon-metal media with nanoengineered attractive forces capable of exceeding 80 g/L volumetric uptake of dihydrogen at –20°C

Nanoengineering the structure evolves into:

Nanoengineering the forces of attraction for dihydrogen

Design the four attractive forces that **act cooperatively** pull dihydrogen into the pore

1. **Van der Waals** attraction to pi cloud of sp^2 (graphene or CNT) carbon surface
2. **Dipole induced-dipole** attraction between a charge separated **(+) metal atom layer** and a **(–) graphene layer**
3. **Charge induced-dipole** attraction near charged metal atoms
4. **Kubas-type interaction** for transition metal atoms

Force design parameter: **Each of the binding energies are intentionally chosen to be inadequate to bind H_2 at room temperature, but collectively will pull H_2 into the pore**

Design for dynamic equilibrium: High density dihydrogen “visits” all sites; **hence H_2 is not bound to any particular surface or any metal atom.**

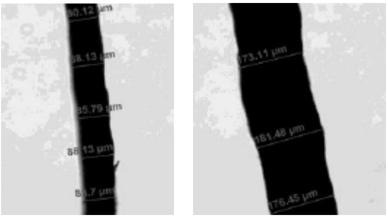
Support structures for metal atoms are not passive – every part participates in attracting H_2

Milestones 2007-08

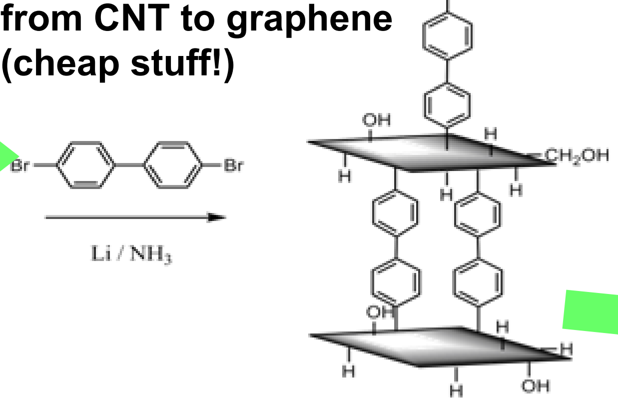
Month/Year	Milestone
Sept-07	Verified 2x enhanced uptake compared to Chahine's rule for nanoengineered pores of carbon nanotubes (done)
Dec-07	Develop new method for making nanoengineered scaffold using lithium ammonia based crosslinking (done)
March-08	Develop new high expansion method for making nanoengineered scaffold using fluorination/defluorination (demonstrated)
July-08	Design scaffold for high volumetric uptake with alternating layers of metal and graphene carbon nanopores (in progress)
Sept-08	Develop “parking spot” for alkali metal & with hydrogen uptake near ambient temp. for graphene and CNT (in progress)
Nov-08	Add capability of making low cost cross-linked graphene scaffolds (started)
Dec-08	Develop first crosslinkers with covalently bound transition metals for hydrogen uptake in graphene @ ambient temp (started)

Approach: All Arrows Point to Room Temperature

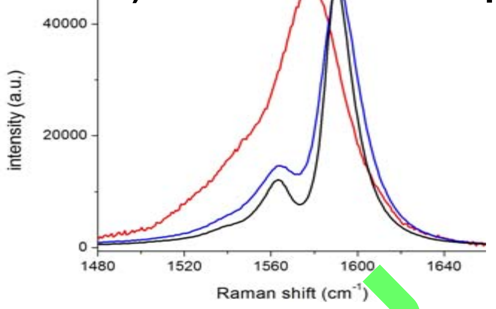
7) New high expansion: Lithium/ammonia



1-4) Transfer nano-expertise from CNT to graphene (cheap stuff!)

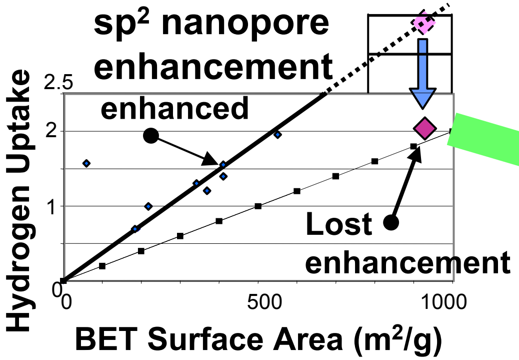


8) Atomic calcium doping

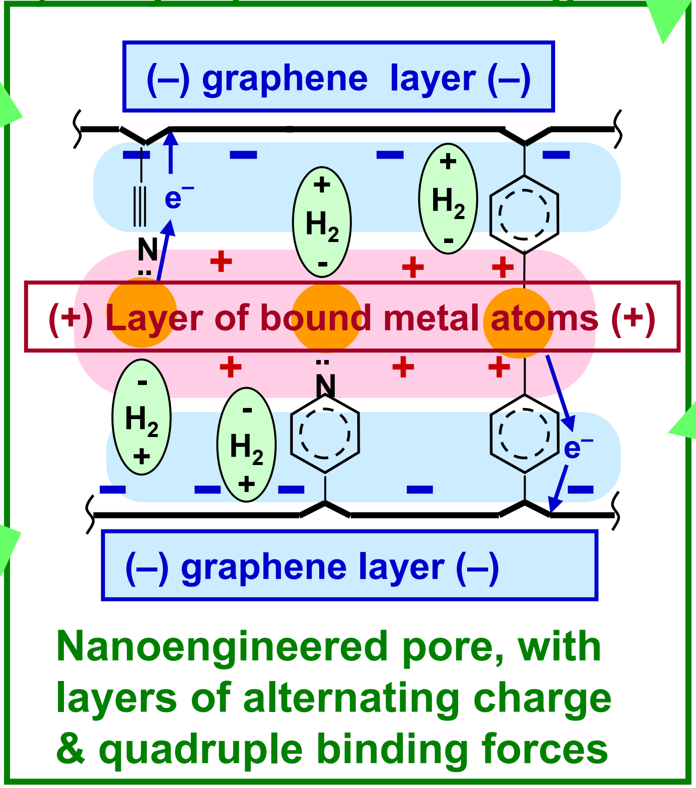


Stabilize

6) Verification of sp^2 nanopore enhancement



11) Many experiments--one goal



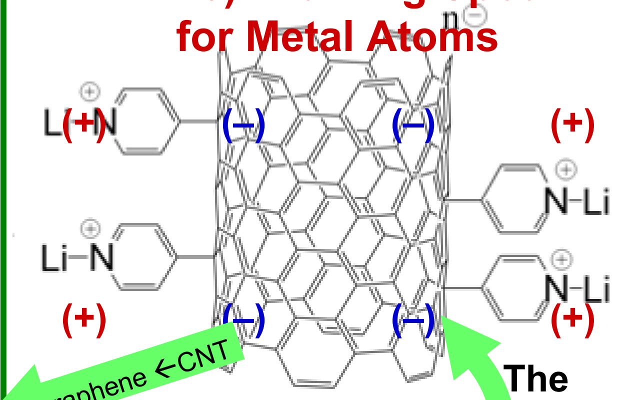
(–) graphene layer (–)

(+) Layer of bound metal atoms (+)

(–) graphene layer (–)

Nanoengineered pore, with layers of alternating charge & quadruple binding forces

10) "Parking Spot" for Metal Atoms

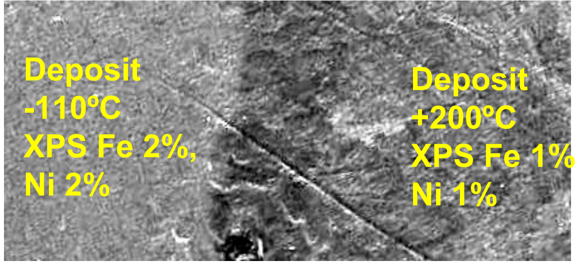


graphene ←CNT

The fix

5) New high expansion: Fluorination/defluorination

9) Monitoring Metal migration



Approach

The main effort is to nanoengineer the forces of attraction for dihydrogen in a layered metal-graphene pore structure for near ambient temperature uptake. Several efforts converge on this central theme.

1-2) Transfer expertise in covalent functionalization of nanotubes to graphene

3-4) Expanded graphene as a new low cost nanoporous media

5) Use fluorination and defluorination + crosslinking to create highly expanded scaffold to accommodate metal atoms.

6) Verify 2x uptake enhancement of the sp^2 carbon pore using F–functionalization to disrupt the sp^2 hybridization as a control – enhancement is lost.

7) Develop lithium/ammonia high expansion with biphenyl linker as a prototype of a **covalent metal-biphenyl crosslinker**

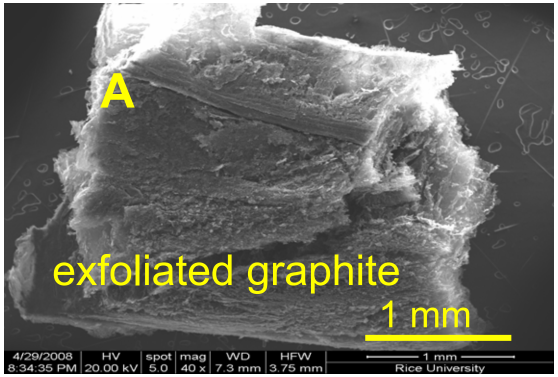
8) Expand scope of metal atom functionalization to others: **calcium**

9) Develop metal migration monitoring method to test stability of metal bonding

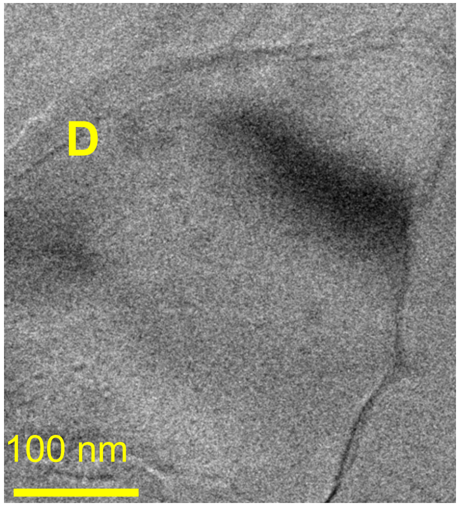
10) Create "parking spots" that covalently bind *metal atoms on a post*; thereby solve the problem of metal migration and clustering.

11) Convergence to a new nanoengineered media: Pores with alternating charge due to interleaved layers of metal atoms and sp^2 (graphene) carbon and engineered quadruple binding forces.

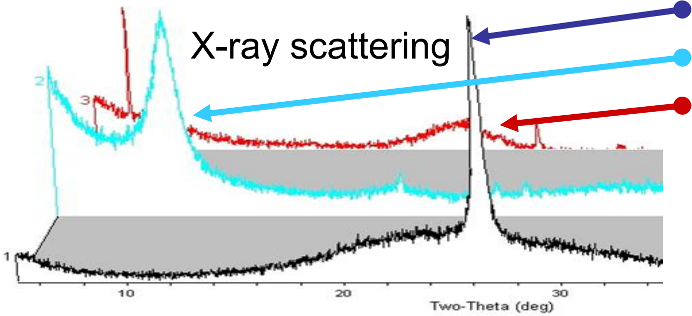
Accomplishment: 1) Graphene reduction & dispersion



Sulfuric acid + oxidizer =
$NaNO_3$; $KClO_3$; $KMnO_4$



Single sheet of graphene oxide viewed by cryo-TEM

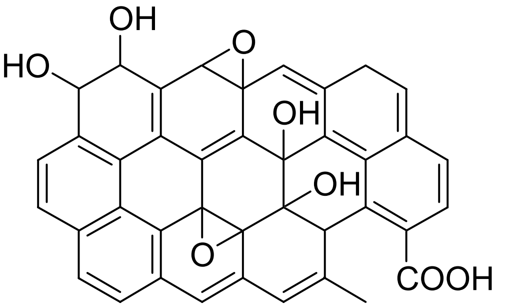


A) graphite

B) graphene oxide

C) graphene-reduced

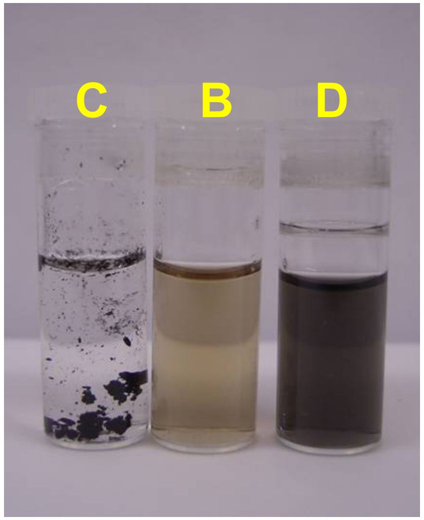
Shows that all sheets are individually separated
2θ becomes much smaller



B) graphene oxide (GO) soluble

C) graphene reduced with hydrazine (insoluble)

D) graphene reduced with hydrazine in surfactant; soluble in micelles



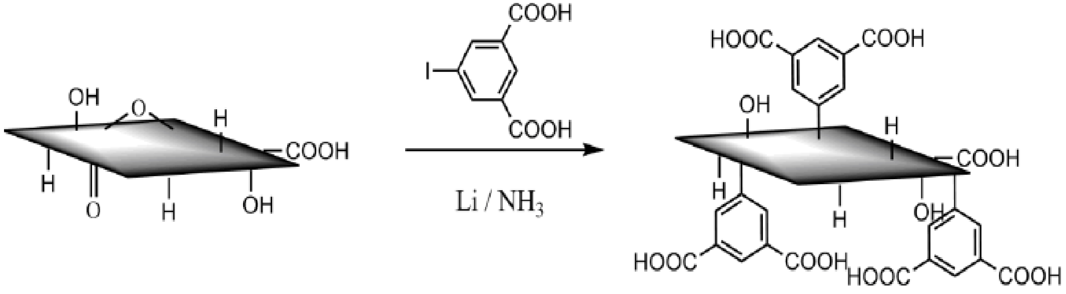
First step to making nanoengineered graphene: X-ray, TEM, and dispersion in water show that each sheet can be separated from its neighbors.

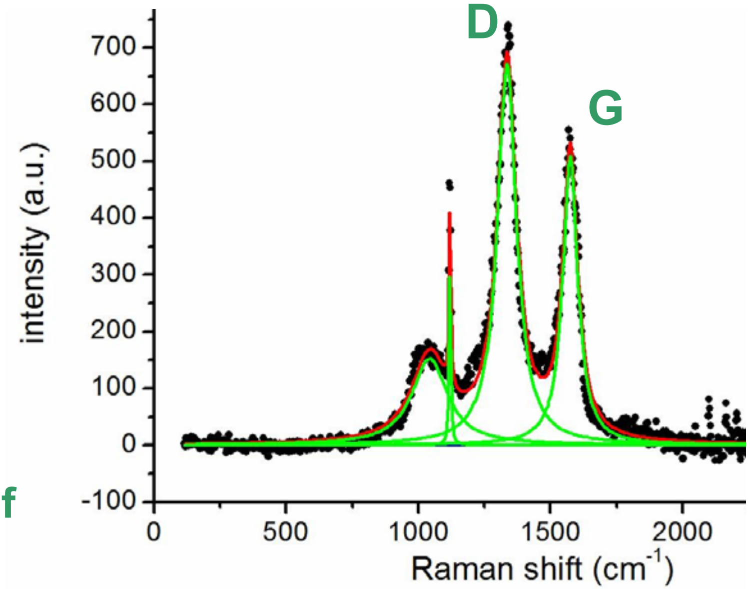
Accomplishment: 2) From CNT to Graphene

Single sheet graphene is the “New kid on the block” for nanoengineered materials [Nature, July 2006], due to oxidation [Yakobson 2007a] Graphene, like SWNT, has superb thermal conductivity. Electrostatic assembly into nano-ribbons has been demonstrated [Sidorov 2007]

Graphite is oxidized with very low cost reagents: sulfuric acid + oxidizers like chlorates or permanganates, to make water soluble graphene oxide (GO).

We have now begun applying well-developed SWNT organic synthesis methods to create carbon-carbon covalent bonding of functional groups to graphene.





Lithium – aryl iodide reaction leads to covalent C–C bonding of isophthalic acid to a graphene sheet.

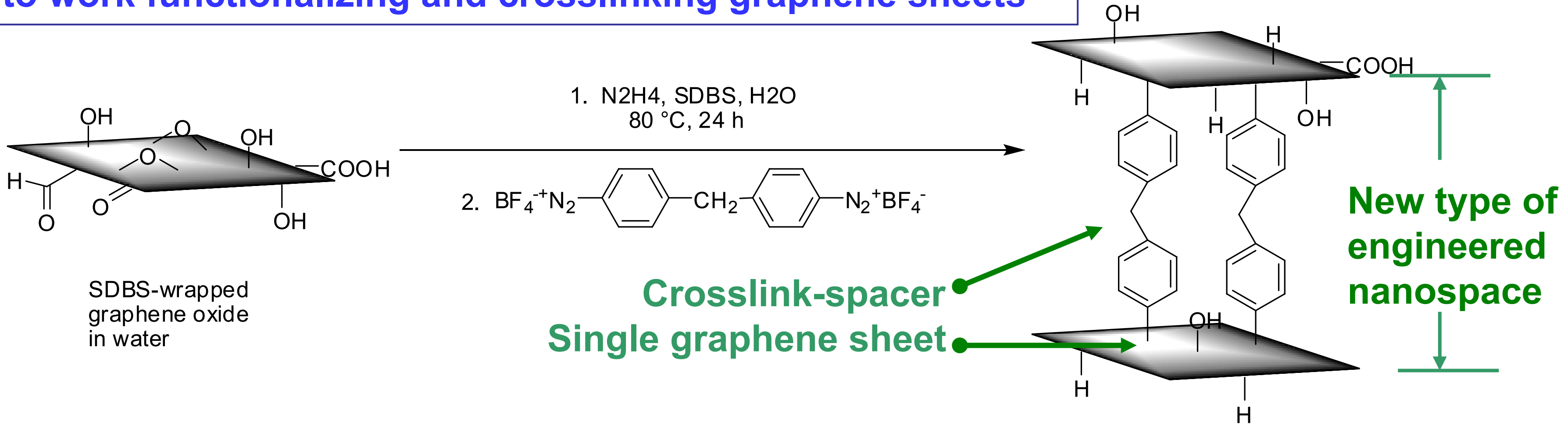
Raman spectra (514 nm excitation) shows a strongly enhanced “D” peak, **due to the new sp^3 hybridization of the graphene.** Green lines = fit to peaks, D:G ratio 1.4:1

Leading expertise in SWNT sidewall functionalization now being transferred to the newborn field of single sheet graphene functionalization chemistry.

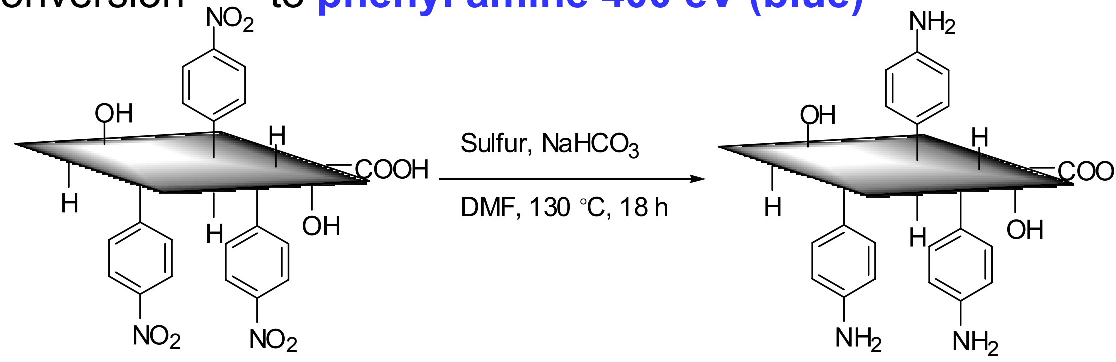
Accomplishment: 3) Graphene Crosslinking

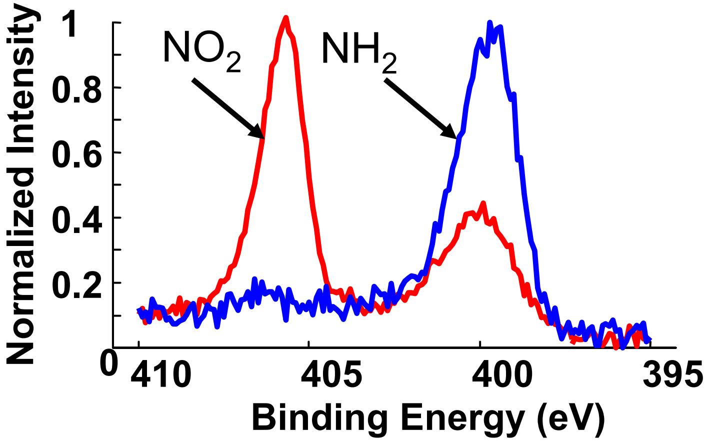
Brand new chemistry: Covalent C-C bonded functionalization of single graphene sheets.

Diazonium chemistry for functionalizing SWNT sidewalls now put to work functionalizing and crosslinking graphene sheets



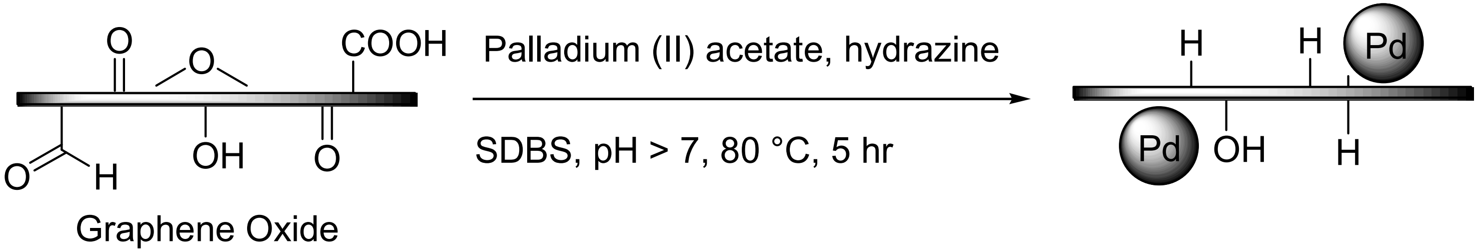
Chemistry on graphene: Metal atoms readily bind to amines XPS data shows **phenyl nitrate at 406 eV (red)** and conversion to **phenyl amine 400 eV (blue)**





Broad knowledge of the chemistry of SWNTs is proving invaluable for rapidly developing single sheet graphene chemistry to make an engineered nanospace for H_2 at RT

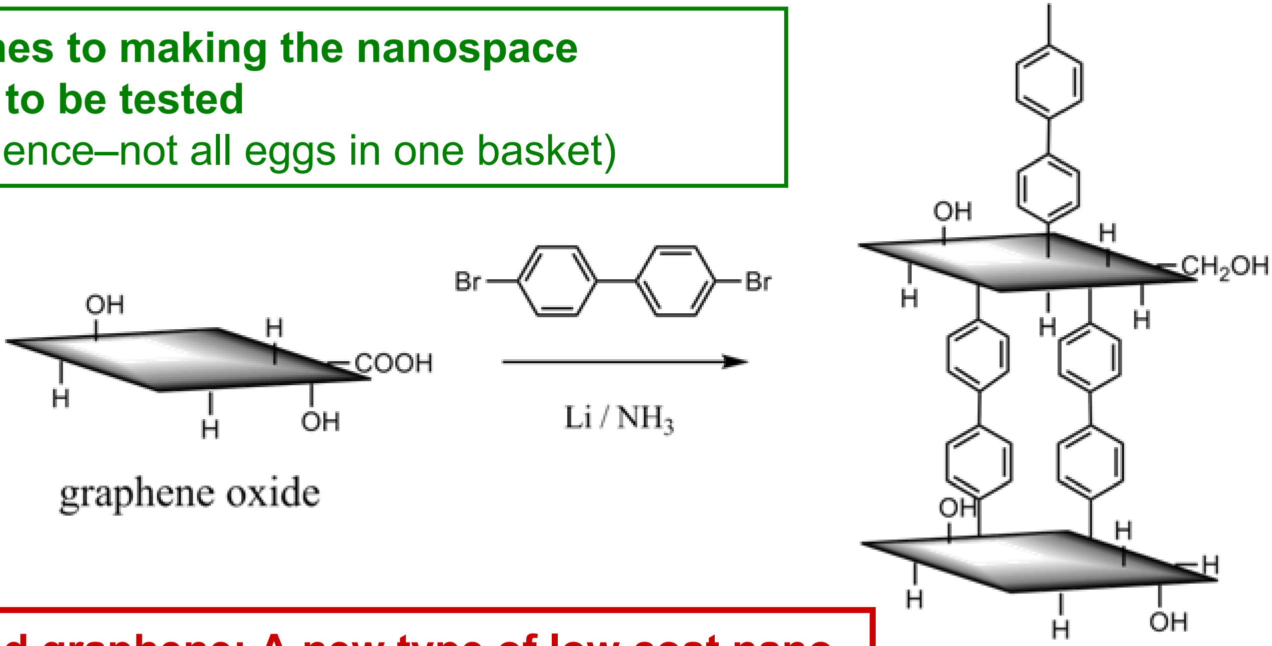
Accomplishment: 4) Graphene metal intercalation



Palladium loading of the graphene is 3atom% by XPS; solution based chemistry
Other experiments have shown 7atom% loading of Pt.
If atoms are mobile on CNT, they are more so on graphene (less sp^3 character); "parking spots" are essential, & this technology developed for SWNT will be transferred to graphene.

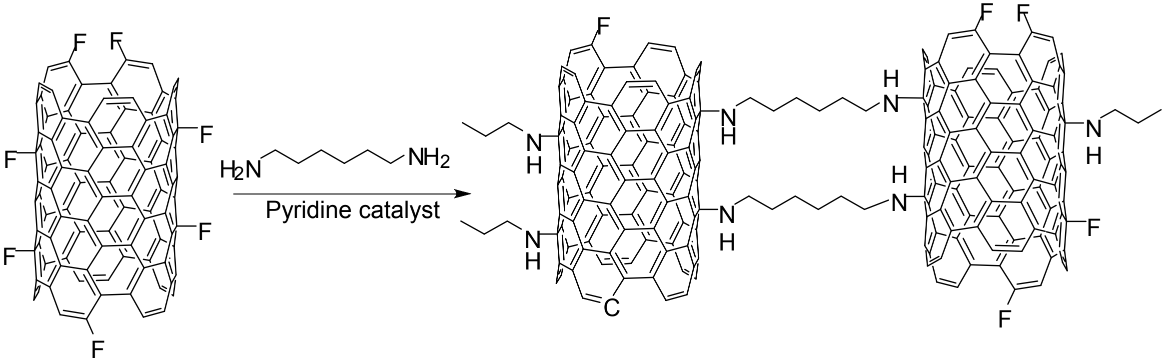
Second of two approaches to making the nanospace graphene scaffold soon to be tested
(lesson from oleum experience–not all eggs in one basket)

Uses same lithium-ammonia & and aryl halide chemistry as for SWNT fiber expansion shown on earlier slide

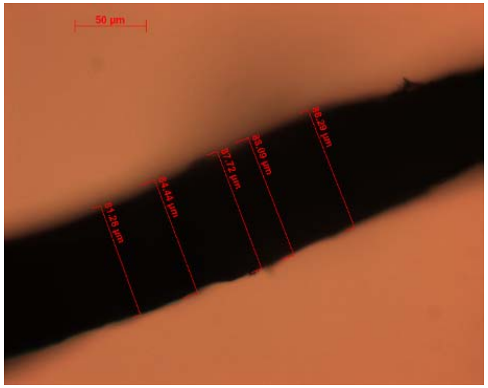


Intercalated and Crosslinked graphene: A new type of low cost nano-engineered scaffold for binding metal and RT uptake of dihydrogen.

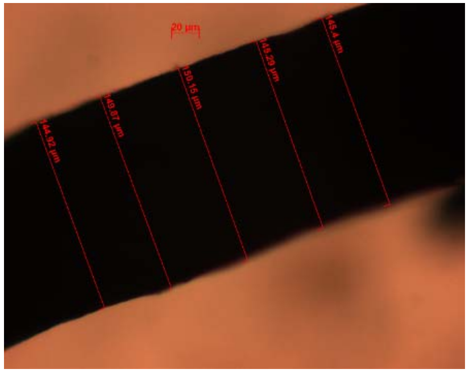
Accomplishment: 5) Fluorination & crosslinking of fiber



Gas phase fluorination apparatus.



Before fluorination 86 μ m

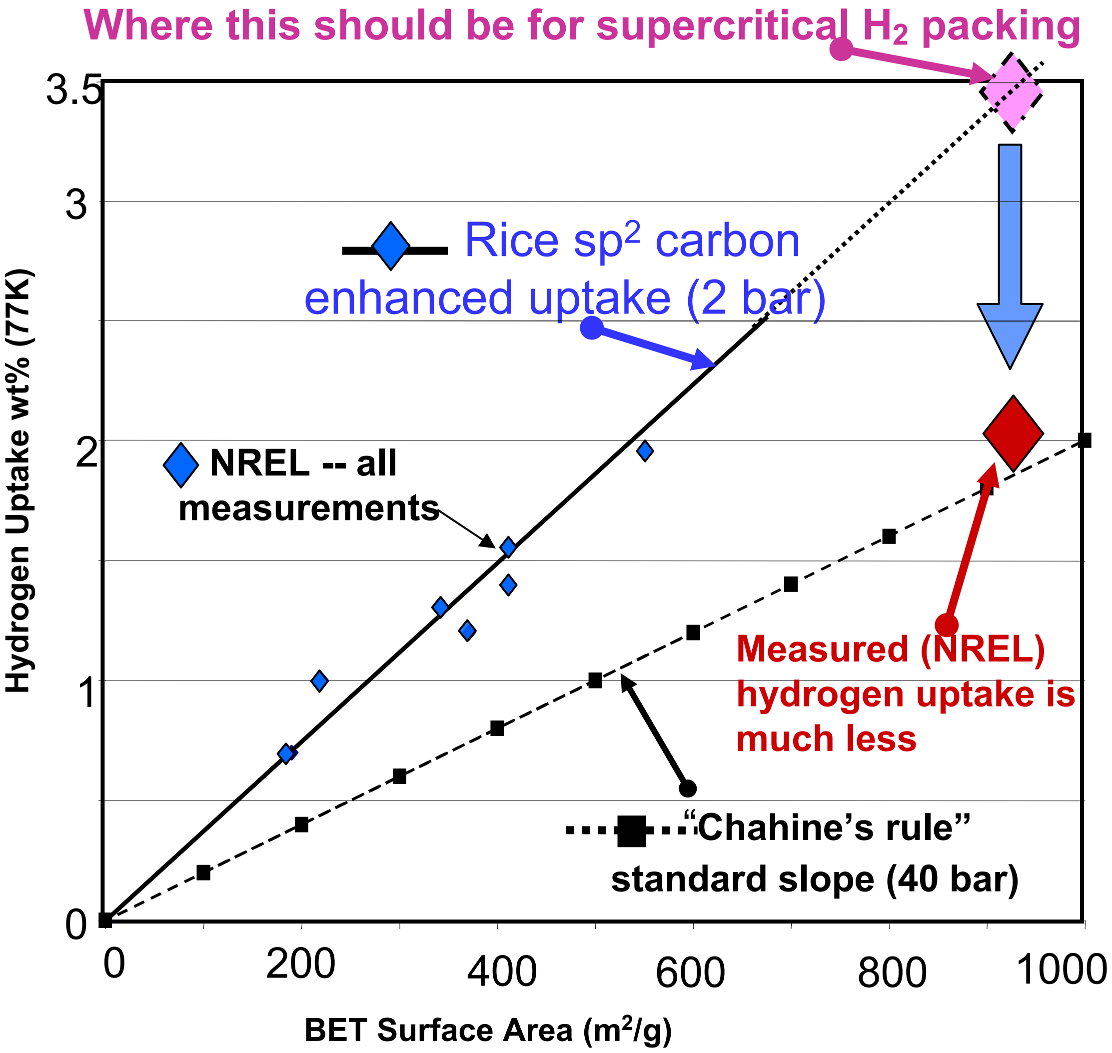


After crosslinking 147 μ m

Longer hexamethylene-diamine bifunctional crosslinkers lead to larger expansion
Expansion corresponds to wall to wall **spacing increased to 1.3 nm**
Fluorine is removed by reduction – This method avoids troublesome oleum solvent
XPS shows 30% fluorine content during expansion; reduced to 1% F_2 after defluorination

- **New method for creating 3-D nanoengineered pore structure with high expansion**
- **Larger bifunctional crosslinkers lead to larger expansion; provides tunable pore size**
- **Well developed for nanotubes, methodology will now be transferred graphene**

Accomplishment: 6) Fluorination & loss of enhanced H_2 uptake


Where this should be for supercritical H_2 packing

Rice sp^2 carbon enhanced uptake (2 bar)

NREL -- all measurements

Measured (NREL) hydrogen uptake is much less

"Chahine's rule" standard slope (40 bar)

- F covalently bonds to surface, with very high coverage, >1:3 F:C ratio
- H_2 uptake far below that expected for a pi cloud nanopore; sp^2 bonding compromised
- Provides a control for the theory of special enhanced uptake of sp^2 pores

Support for the "nanopump" concept

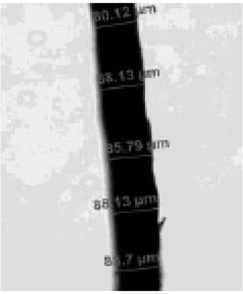
Slit pores in graphene, enhanced equilibrium constant - theory [Patchkovskii 2005].

C_{60} — graphene separators - theory [Kuc, Nano Letters 2007]

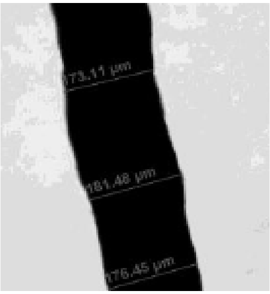
Supercritical uptake on sp^2 carbon, expt. H_2 [Iijima 2003], Ar, Kr [Do 2003]

Uptake per unit surface area (SA) doubles for intact pi cloud, control experiment verifies enhancement is lost when the special nature of pi cloud is compromised

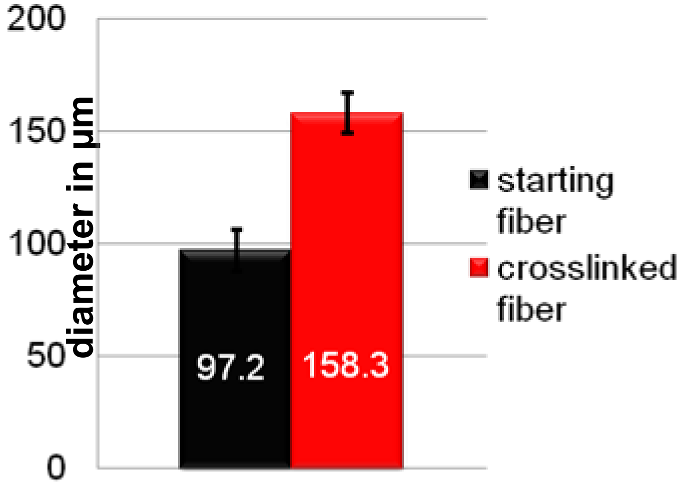
Accomplishment: 7) Lithium expansion & crosslink



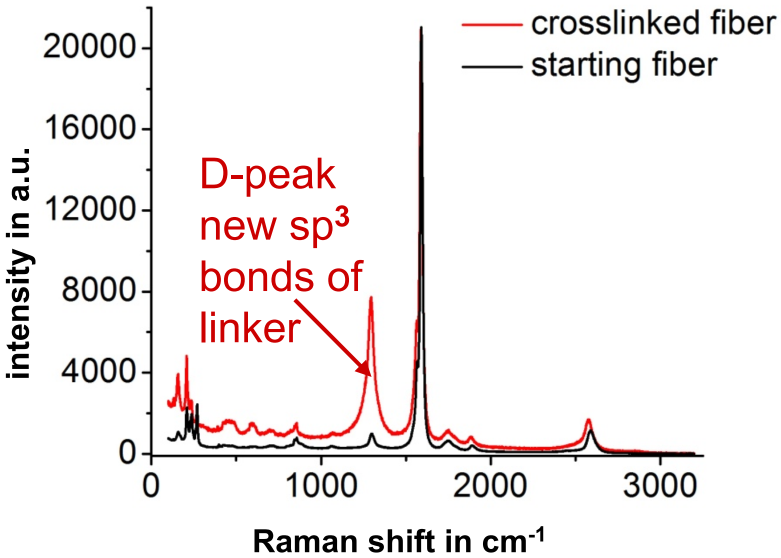
Starting fiber

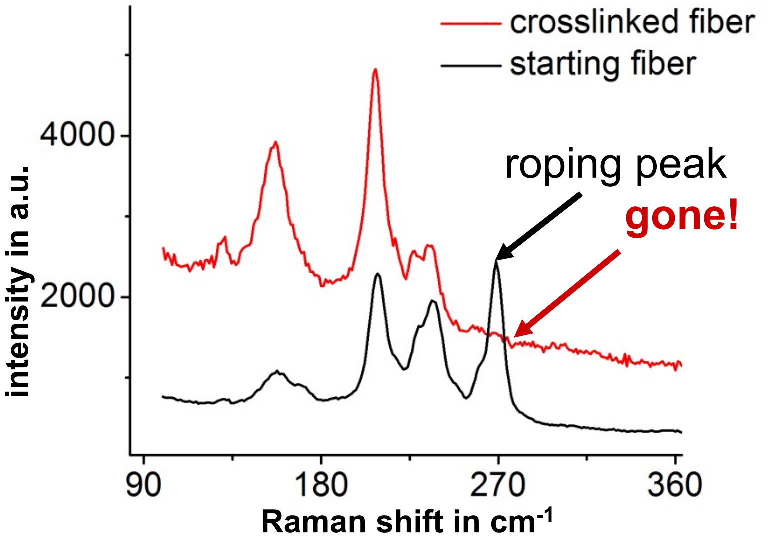


Expanded fiber



New dibromophenyl cross-linker developed
Cleaner expansion with new low-cost reagent

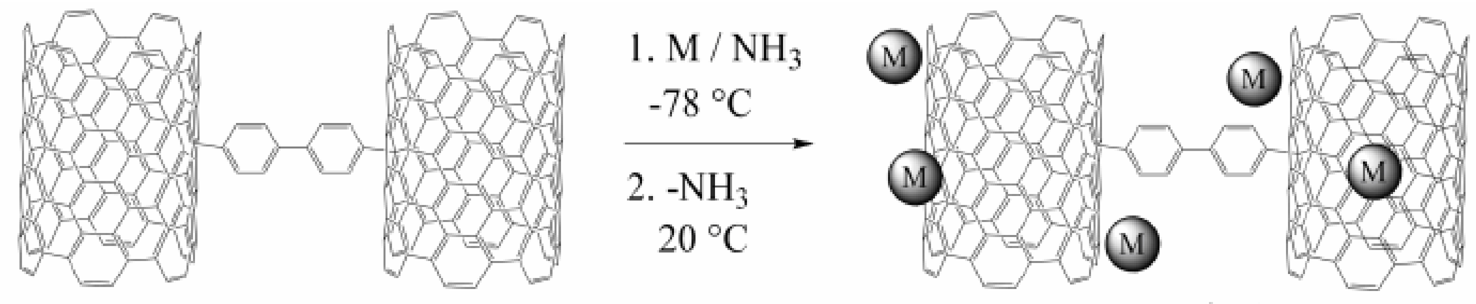


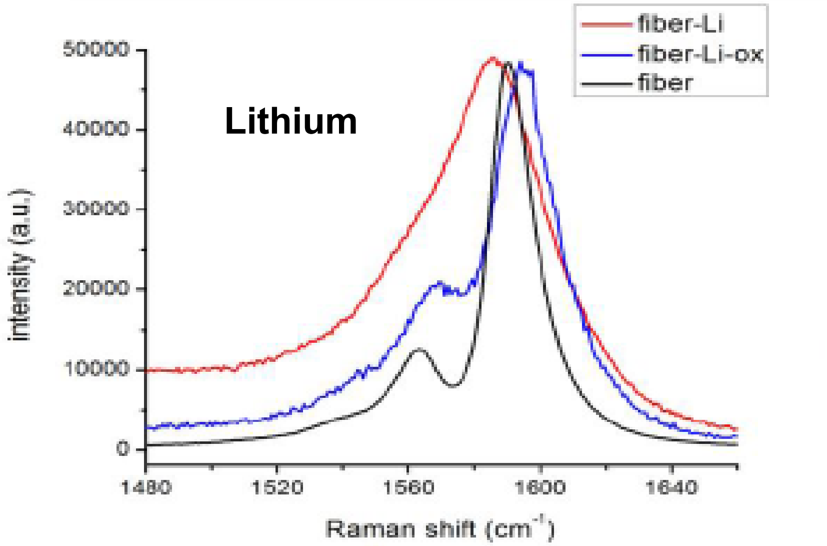


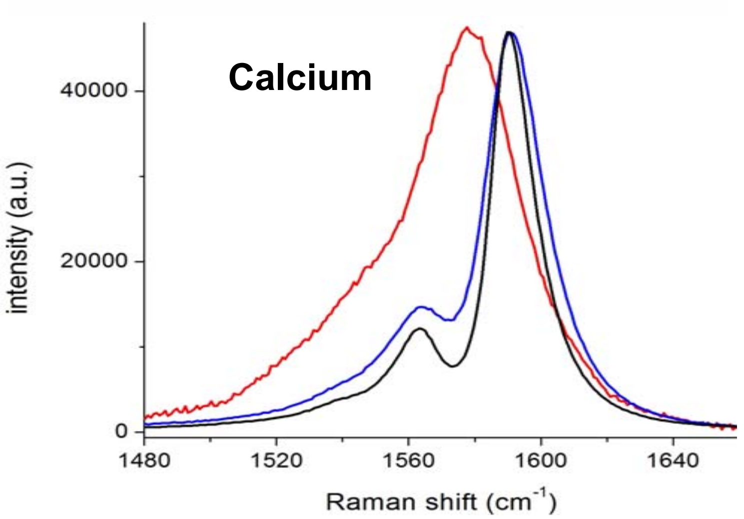
Raman spectra: Big increase in D-peak shows covalent bonding established
Disappearance of the "roping peak" [Doorn 2005] → **nanotubes are all cleanly separated**

Reliable expansion makes scaffold ready to accept metal atoms for H_2 uptake at RT

Accomplishment: 8) Calcium doped CNT fiber







Expanded CNT fibers are doped with lithium or calcium in ammonia, 785 nm Raman excitation

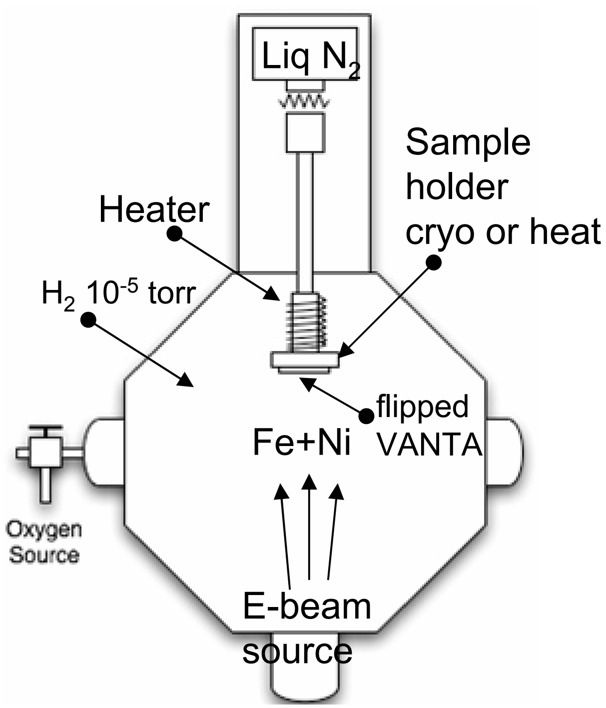
The initial (black trace) G-peak shifts to lower frequency, which shows **electron charge transfer (red trace) from the metal to the sidewall**. **It shifts back (blue trace) when the metal is oxidized and decouples**. The large shift is indicative of strong electron transfer from individual atoms.

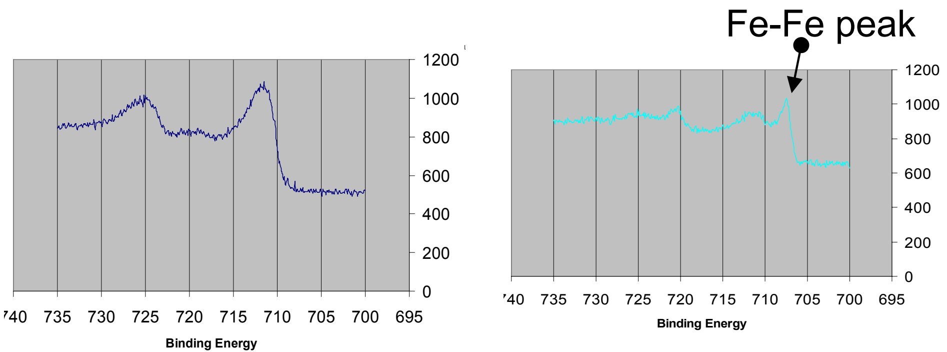
Not yet perfected; broadening of the peak indicates the metal has not fully penetrated the fiber to the core.

Calcium metal atom attractive as a host for ambient H_2 uptake (ORNL theory)
Graphene likely to be too "slippery" and a parking spot will be needed (expt 10)

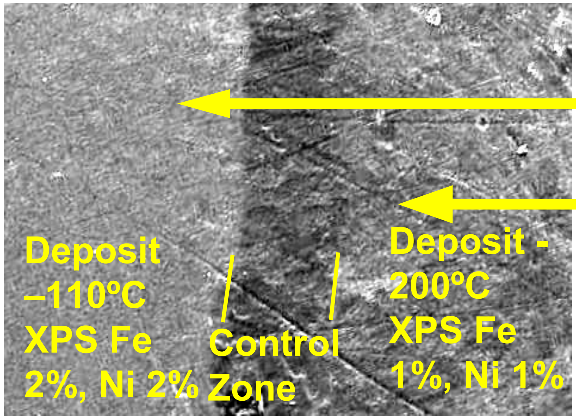
Accomplishment: 9) Monitor for metal migration

Advantage of doping a with metal is lost if the metal can migrate; predicted [Yakobson 2007b].
Apparatus has been constructed by undergraduates(!) at Rice to test for migration of Fe & Ni on carbon
It is exposed to metal H_2 at different temperatures, & subsequently oxidized to lock the metal in place.
SEM and XPS are used to observe the clustering of the bare metal atoms





Left spectra, 25°C. Right spectra, 600°C
XPS data shows extra Fe-Fe peak on right due to clustering



SEM of VANTA - CNT

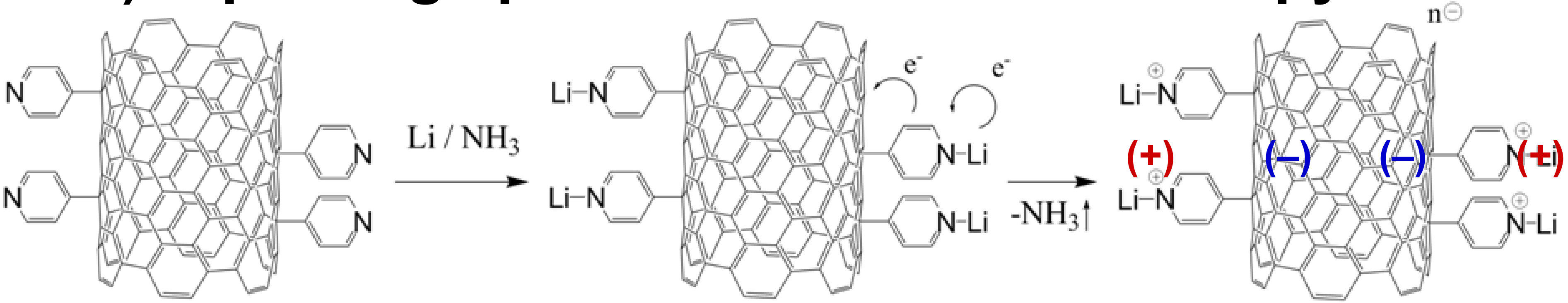
Low temp. deposit stays **bright**, metal does not migrate

High temp. deposit, metal migrates down into nanotubes, does not scatter e¯; **image becomes darker**

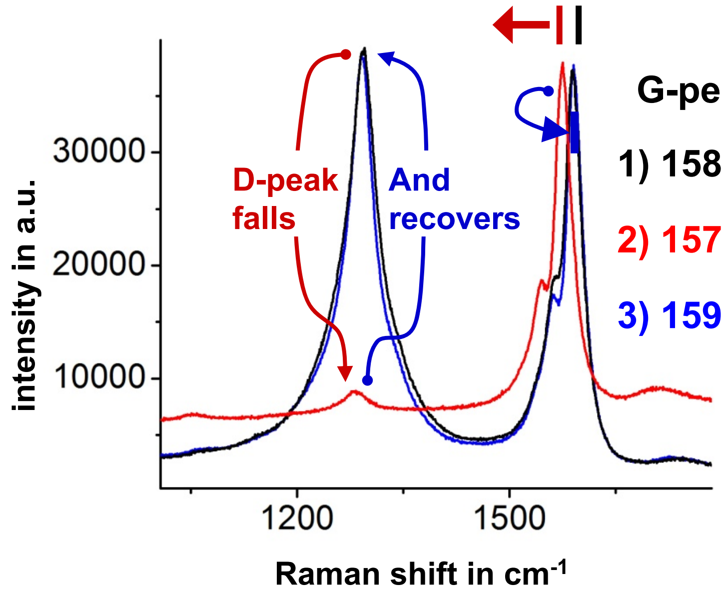
Darker stripe in middle = no metal

New apparatus provides temperature control for testing metal atom migration in H_2, which will become ineffective if clustered. Iron and nickel both migrate at elevated temperatures, not at cryogenic temperatures; mobility is probably even higher in graphene, which now needs to be tested

10) A parking spot for metal atoms: Li on pyridine



Nanotubes covalently functionalized with pyridine; Lithium atoms bind; e^- has charge transfer to sidewall



G-peak shift

1) 1589.7 cm^{-1}

2) 1575.3 cm^{-1}

3) 1590.6 cm^{-1}

Raman spectra (785 nm excitation)

1) Functionalized starting material

2) Add lithium:

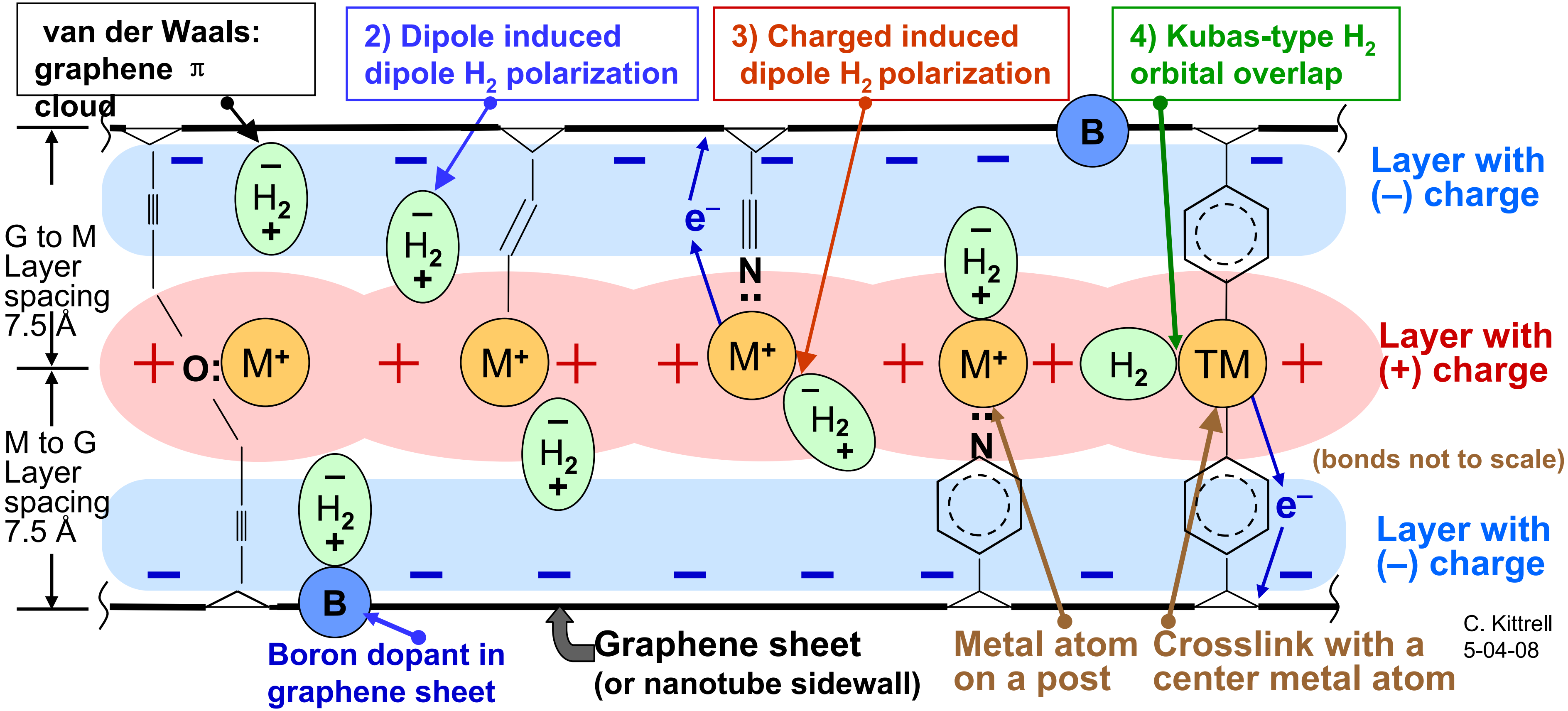
- **2a) Big Eklund shift of 15 cm^{-1}** [Eklund 2002]
- **2b) No G-peak broadening – uniform doping**
- **2c) D-peak nearly gone; probable loss of sp^3**

3) Oxidize the lithium, & the D- and G-peaks return to normal

G-peak shift shows that (–) charge moved to sidewall and caused a decrease in the Raman shift; lithium tends to transfer a partial charge to the host when it is bound, becomes $Li^{+1/2}$ [Namilae 2007] (ORNL) **Subsequent oxidation binds the lithium, and hence removes the charge.**

New method to anchor metal atom prevents diffusion, charge transfer still good; anchor probably even more important for graphene, which has the least "sticky" sp^3 character.

11) Nanoengineered slit pore with metal-enhanced uptake



C. Kittrell
5-04-08

Concept:

Alternating layers of charge with metal atom electron donors and graphene receptors for H_2

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

Charge transfer fosters alternating (+) and (–) charges in the metal/graphene layered pore

"Metal atom on a post" provides sufficient density of metal atoms in the middle layer & e^- doping

Four cooperative forces of attraction operating on dihydrogen: 1) Van der Waals, 2) Dipole induced dipole, 3) Charge induced dipole, 4) Kubas-type binding for transition metals

Accomplishment: Design of nanoengineered forces using anchored metal atoms

Key design features:

Alternating charged layers **(+) metal** and **(–) sp^2 graphene carbon**

Problem of mobility and clustering of metal atoms are **mitigated by a covalent anchor,** 100% of metals are chemisorbed, and 0% of the hydrogen is chemisorbed. Cycling without degradation is feasible.

Enhanced attraction into nanopore activates "nanopump" concept [Patchkovskii 2005]; →thermodynamically driven packing the pores with a high density and mobile hydrogen gas that encounters all sites.

There is one underlying assumption: That it is possible to design the structure such that the H_2 experiences a composite attractive force which yields at least $-\Delta F = 13$ kJ/mol. This is the force that switches on the nanopump. Once the pump turns on, H_2 uptake is just geometry and thermodynamics.

Forces of attraction are now also nanoengineered design parameters →the scaffold becomes a full participant in RT uptake & not just a passive support.

Four types of attractive forces combine to pull dihydrogen into the pore:

1. **Van der Waals** attraction to pi cloud of sp^2 carbon surface → **adjustable** by the radius of curvature of the CNT [Chen 2005] (Air Products) or side groups to add strain to graphene
2. **Dipole induced-dipole** attraction between a charge separated **(+) metal atom layer** and a **(–) graphene layer is adjustable** a) High doping the graphene sheet with **boron** such as BC_3 ; b) Ease of electron transfer across the supporting "post"
3. **Charge induced-dipole** attraction @ charged metal atoms → **adjustable** by selection of electron affinity and ionic radius of the metal atom
4. **Kubas-type interaction** for transition metal atoms → **adjustable** by selection of metal; avoid those with strong binding that can dissociate the H_2 [Kubas 2001]

New Paradigm: Multiple tailored binding forces, nano-pores filled with high density H_2
Avoid designs with strong H_2 binding to metal atoms → risk of dissociation
Surface physisorption is inadequate for volumetric goals, use H_2 filled pores.

Accomplishment: Designed thermodynamic nanopump

How much free energy should we choose to operate the "nanopump"? -ΔF = RTlnK

-ΔF = 13 kJ/mol; T = 253°K = –20°C; Equilibrium constant **K_f = 35** (corrected for non-ideal gas);

Fill pressure P_{ext} = 100 bar; internal "pressure" P_{int} = 3500 bar (density equivalent); calculation restricted to modest 20% extrapolation of fugacity data tables (max 3000 bar) [Shaw 1964]

H_2 molecules are not "squeezed": Volume available per H_2 is 33 Å^3; 2.4x larger than hard sphere. Available space d = 4Å; collision diameter d = 3Å [Kowalczyk 2005] & Feng Ding (Yakobson PD);

Additional entropy of confinement of H_2 in the pore (not bound), ΔS range 4–11 J/mol-K [Patchkowskii 2005]

Calculated volumetric capacity at 253°K = 86 g/L H_2 = 2.9 kWh/L

Gravimetric estimate—optimum metals not known—use K on post and Ru in crosslinker→11.4wt%

Residual hydrogen estimated 4.5% not available:→ **deliverable 81 g/L and 10.9wt%**

Estimate for (5,5) cloned SWNT scaffold → has approx. same capacity as metal-graphene scaffold

Options for substantial increases volumetric capacity:

Increase spacing: Our chosen spacing of 1.5 nm double layer is close to 1.3 nm expansion we obtained; larger layer spacing preferred (Channing Ahn recommended 9 Å to 10 Å); this increases unit cell height + 0.3 nm to 1.8 nm; no increase in graphene sheet weight/volume (just longer crosslinkers)

Higher density H_2: 1.7x higher H_2 densities measured by [Mills 1977]; 120 g/L volumetric predicted low temp. [Kuc 2007] but not readily calculated – lack of data on HP non-ideal H_2 gas. K is exponential in free energy, doubling for an increase –ΔF by only 1.5 kJ/mol. For –ΔF increased to 17.5 kJ/mol, K increases 8-fold(!)

To obtain 120 g/L H_2: Gain 7% from increased pore spacing and 30% more density by increased pore pressure (less than half of [Mills]); H_2 will occupy a volume of a 3.7 Å diameter sphere, still much larger than the 3 Å hard sphere, & even larger than 3.5 Å "standard" surface spacing; → 120 g/L uptake near RT appears possible.

Thermodynamically driven compression of H_2 into nanoengineered pores is an excellent approach for the high volumetric uptake at 20° C needed for 2015 goals

Accomplishment: Design for Metal-Enhanced Uptake

Nanoengineering the force of attraction: Choices

Choose metal atoms that have weak attraction inadequate to bind at H_2 RT, "H_2 unbound", no energy barrier for fast kinetics, low residual retention. Divalent metals like calcium-on-a-post may be "capped" with CH_3 or the like to prevent H_2 dissociation; covalently bonded Li does not dissociate H_2.

Fill pores; eliminate surface uptake; no multilayer H_2 coating needed, see [BES Workshop 2003]

Prefer metals for which accidental oxidation is reversible *in situ* (e.g., Fe, Cu), for unlimited cycling

Binding energies for attractive forces – many options to collectively reach $-\Delta F = 13$ kJ/mol

1) **Van der Waals**: up to **10 kJ/mol** theory [Patchowskii 2005]; expt. [Eklund 2002](Penn State)

2) **Dipole induced-dipole** TBD by ORNL partners, boost it with **C_3B-doping** (Penn State)

3) **Charge**: **$Li^{+1/2}$** bonded aliphatic moiety, **0.09 eV** for H_2, Calculated [Namilae 2007] (ORNL)

4) **Kubas-type: H_2 + Cu 0.33eV**, **Mn 0.24 eV**, Calculated [Yildirim 2007](NIST); H_2-Cu^{2+} observed [Brown-2007](NIST)

Excess capacity for this alternating layer metal–graphene media

H_2 storage capacity compared to "empty" tank = 10 g/L also @ 100 bar, 253°K; (86–10)/86 g/L = 88% excess capacity; 81 g/L x 88% = **71 g/L excess delivered.** Gravimetric 10.9wt% x 88% = 9.5wt% excess delivered

New potential for collaboration:

Can adapt to electronegative species: F^- (Air Products); or BF_4^- (R H Hauge, Rice)

Can add **boron doping** (Penn State), enhances charge separation.

Useful as a scaffold for **metal hydrides,** with bound **metal-alloy particles** in place of atoms. (Ongoing discussions with Channing Ahn, Caltech)

Alternating layer design sent to Geohegan group (ORNL); expertise in charged structure computation

Plan to contact NIST for neutron analysis of layered graphene structure

"Nanoengineering" now expanded to encompass design of force structure of H_2 uptake
Collaboration with partners will help us explore this new concept

Project Summary

Technical Accomplishments and Progress

1-2) Expertise with SWNTs adapted to functionalization of single graphene sheets

3-4) Crosslinking and metal uptake as first steps to make a low cost nanoengineered media starting with graphite.

5-6) Demonstrated that 2x enhancement for uptake at 77K is due to properties of nanoengineered sp^2 pore; "normal" Chahine's rule behavior returns when fluorination disrupts pi cloud. Developed crosslink and defluorination methods

7) New lithium/ammonia crosslink method, individual – nanotubes are well separated, new low cost reagent. This chemistry is being adapted to graphene crosslinked scaffold

8) **Calcium doping showed large electron transfer to sp^2 carbon CNT sidewall**

9) Apparatus constructed to monitor metal atom migration & successfully tested.

10) Lithium attached to pyridine-functionalized nanotubes; demonstration of the "parking spot" for preventing diffusion of metal atoms; good charge transfer; graphene next.

11) Convergence: Developed concept of alternating charged layers of metal and graphene with four cooperative binding forces; H_2 unbound; projected volumetric delivered 81 g/L.

All experiments point toward creation of nanoengineered attractive forces which are feasible for metal & sp^2 carbon media that will have high volumetric uptake of dihydrogen at ambient temperatures.

Future work

FY08

- Continue alkali metal functionalization work. Transition to graphene
- Develop graphene expansion and crosslinking methods → transfer top notch expertise in SWNT sidewall chemistry to (new) low cost single sheet graphene.
- Transfer the enhanced hydrogen uptake concept of the CNT scaffold to the metal-graphene scaffold near RT, i.e., make the "nanopump“ for dihydrogen work at RT like it did at 77K;
- Begin hydrogen uptake tests on nanoengineered pores with anchored metal atoms, add temperature programmed desorption *in-situ* for rapid sample testing
- Continue tests to determine if a hydrogen atmosphere induces transition metal mobility at moderate temperatures or affects chemisorbed metals.

FY09

- Scale up the production of graphene scaffold; raw materials are cheap and abundant
- Incorporate transition metals into cross-linkers to help form the alternating layers of metal and graphene/ nanotube Determine which ones are best suited. Measure dihydrogen uptake; watch out for H_2 dissociation; prevent by adding “caps”.
- Determine if better thermodynamic data can be obtained for estimating uptake with a larger equilibrium constant for H_2: Stronger nanopump = higher internal pore "pressure" → 5 to 10 kbar; test uptake
- Does hydrogen behave like a high pressure gas in the nanopore, or does it bind to specific sites? Determine the physical chemistry (theory and experiment) of the concept of nanoengineering the fourfold attractive forces of the alternating metal—graphene nanopore.

Summary Table

On-Board Hydrogen Storage System Targets
(**Data is based on material only, not system value)

Storage Parameter	**Units**	**2010 System Target**	**FY06 materials** Ox-SWNT**	**FY07 nanoengineer fiber****	**FY08 nanoengineered graphene****
Specific Energy	kWh/kg (wt% H2)	**2.0** **(6 wt.%)**	**0.97** **2.9 wt%**	**0.67** **2.0wt%**	**Calculated 3.5 kWh/kg** **10.9wt%** **9.5wt% excess**
Volumetric Energy Capacity)	kWh/L g/L	**1.5**	**0.97**	**Density = 1** **0.67**	**Calculated 2.7 kWh/L** **81g/L** **71g/L excess**
Desorption Temperature			>77°K	>77°K	Calculated ≥ 253°K
Plateau Pressure			Fit to 30 bar	Measured at 2 bar	100 bar fill

Notes:
FY06: Oxidized SWNT material, predates nanoengineering; isotherm at two bar, extrapolated to 30 bar.
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)
FY08 Calculated gravimetric using K atom on post and Ru crosslinker (delivered)
Excess is in addition to the capacity compared to no media at 100 bar, –20°C.
A cloned (5,5) SWNT fiber with similar metal atom functionalization calculated to have similar H_2 G&V

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