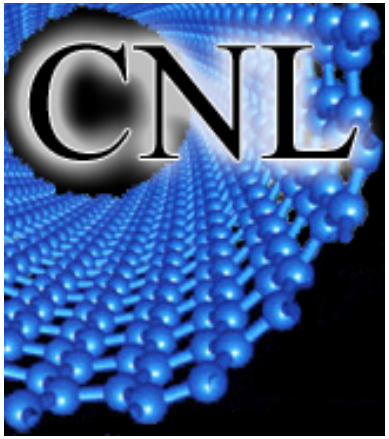
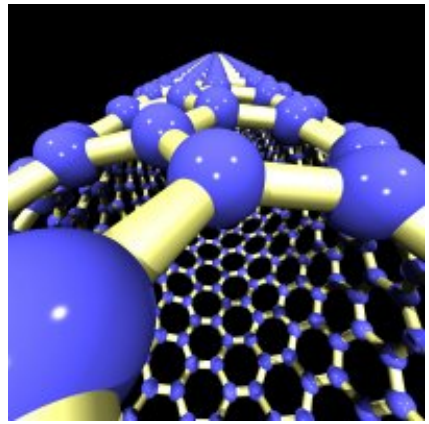




Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

James Tour

Rice University

May 18

(With R. Hauge, C. Kittrell, H. Schmidt, W.-F. Huang and M. Pasquali)

Project ID
#ST26: Tour

Overview

Timeline

- Start-Feb 2005
- Finish-Jan 2010
- 20% complete

Budget

Total project funding

- DOE share $1,715,990
- Contractor share $428,997
- Funding received in FY05: $300,000 plus $75,000 cost share
- Funding for FY06: $250,000 plus $63,000 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, Air Products, Duke, Penn. State and Oak Ridge National Lab

Objectives

- Overall: Develop nanostructures and nanoengineering processes that enable synthesis of materials that can be used to meet the 2010 DOE gravimetric (6 wt%), volumetric (45 g/L) hydrogen storage system goals, with excellent uniaxial thermal transport properties.

- **2005:** Develop processing to produce specific types of nanomaterial structures with increased available surface area
  - –Develop carpet growth, spun fibers, and cloning methods
  - –Develop and test bulk processing methods with improved porosity that increase hydrogen sorption over presently available materials.

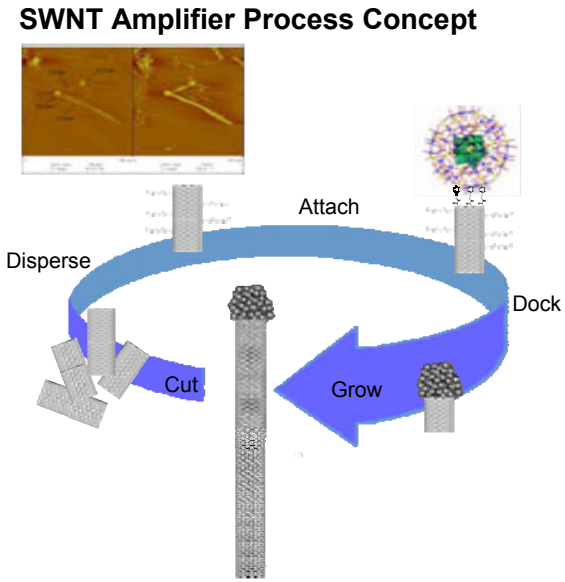
- **2006**: Develop methods for 3-D nanoengineering dense arrays of SWNT carpets and fibers
  - –Design, test and produce these nanoengineering arrays with specific pore sizes for high hydrogen sorption capacities (>4 wt% and 30 g/L uptake)

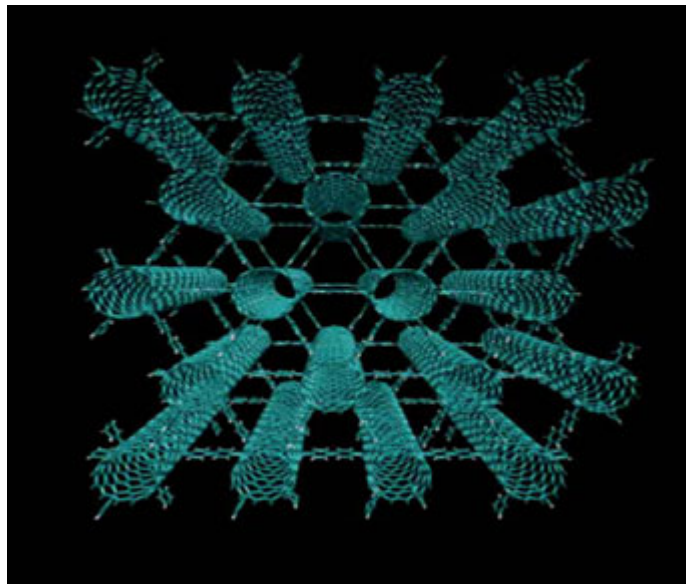
- **2007**: Optimize nanoscale engineering for hydrogen uptake, include cloning, fiber spinning, carpet growth, and pore size
  - –Develop lithium intercalation methods for room temperature hydrogen storage
  - –Scale up fiber production by 10x and carpet growth by 100x to provide for a large number of laboratory scale tests

- Achieve **6 wt% and 45 g/L** H2 uptake on pure fibrous SWNT media at 77°K
- Achieve **6wt% and 45 g/L** H2 uptake on Li: SWNT media at room temperature

Approach

- Cloning SWNT
- Increase Surface Area and optimize pore size for hydrogen storage





Cloning:

Develop techniques that can isolate specific types of SWNTs and other nanostructures that have been demonstrated to have high hydrogen sorption capacities.
Develop cloning techniques that enable exact duplication with high yields of desired nanostructures

Nanoengineering:

Develop processing that creates nanostructured materials with the optimum pore sizes (geometries) needed for maximum hydrogen storage capacity.

Approach

- **Develop additional nanotube production methods: various types of carpet growth, also know as vertically aligned single wall carbon nanotube arrays**
- **Nanotubes show excellent uniaxial thermal conductivity, nearly that of diamond, and these carpet nanotubes, hundreds of micrometers long, will likely be the best**
- **Nanoengineering will be used to obtain the ideal pore size for hydrogen storage. Uniform pore sizes will provide the best combination of highest wt% and highest density by not wasting space**
- **Develop nanoengineering that enables optimum nanostructured materials to be held in space with essentially 100% available surface area (>2300 m^3/g) for maximum gravimetric and volumetric hydrogen storage capacities**
- **Spun fibers will be arrayed into aligned bundles to preserve the uniaxial thermal transport exhibited by individual SWNTs**
- **This fibrous media will also be used to provide good gas transport along the axis. The loss of thermal conductivity typical of granular media is mitigated**
- **Add intercalated lithium to raise the binding energy to more than 7 kcal/mol, for 6 wt% H2 uptake at room temperature**

Background

Problems we have addressed concerning Single Wall Carbon Nanotubes (SWNTs)

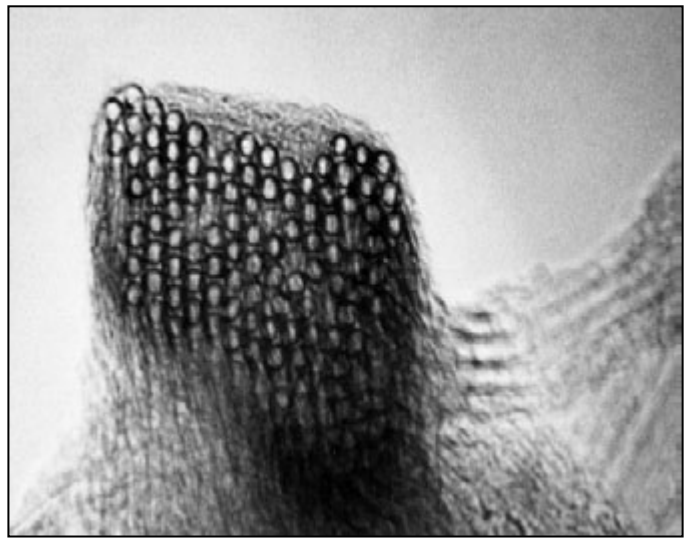
(a) There is little control over nanotube (n,m) type to maximize the adsorption properties

(b) The nanotubes are bundled which makes the sidewalls inaccessible

c) Randomly oriented unbundled individual nanotubes have a density that is too low

d) Forced expansion of the bundle by high pressure filling is undesirable (for any carbon adsorbing media)

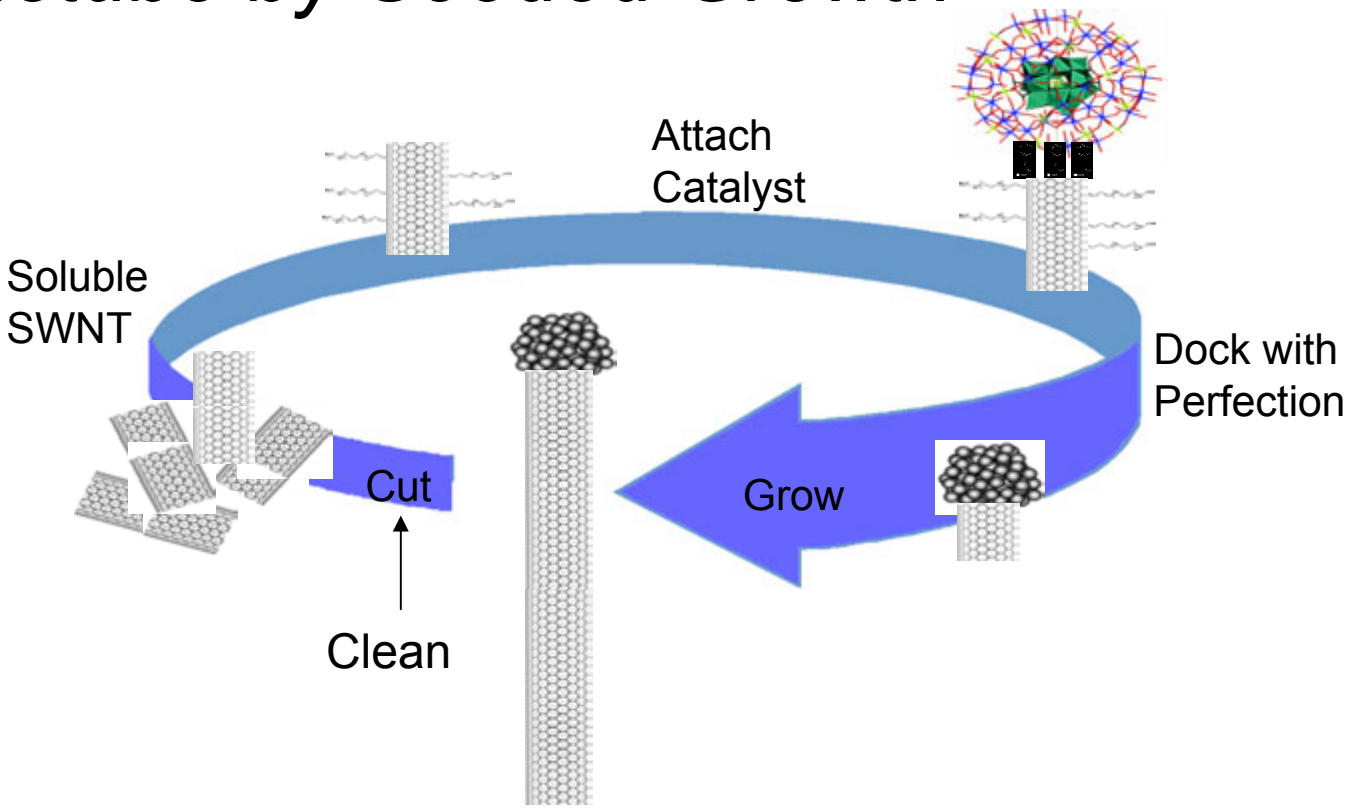
e) Hysteresis & macroscopic expansion on every cycle→ potential for wear and deterioration of media



Bulk nanotubes from a reactor show the expected inadequate H2 uptake, as has been observed by this and other research groups.

They must be nanoengineered to provide adequate surface area and density.

SWNT Reproduction of a Single Type of Nanotube by Seeded Growth



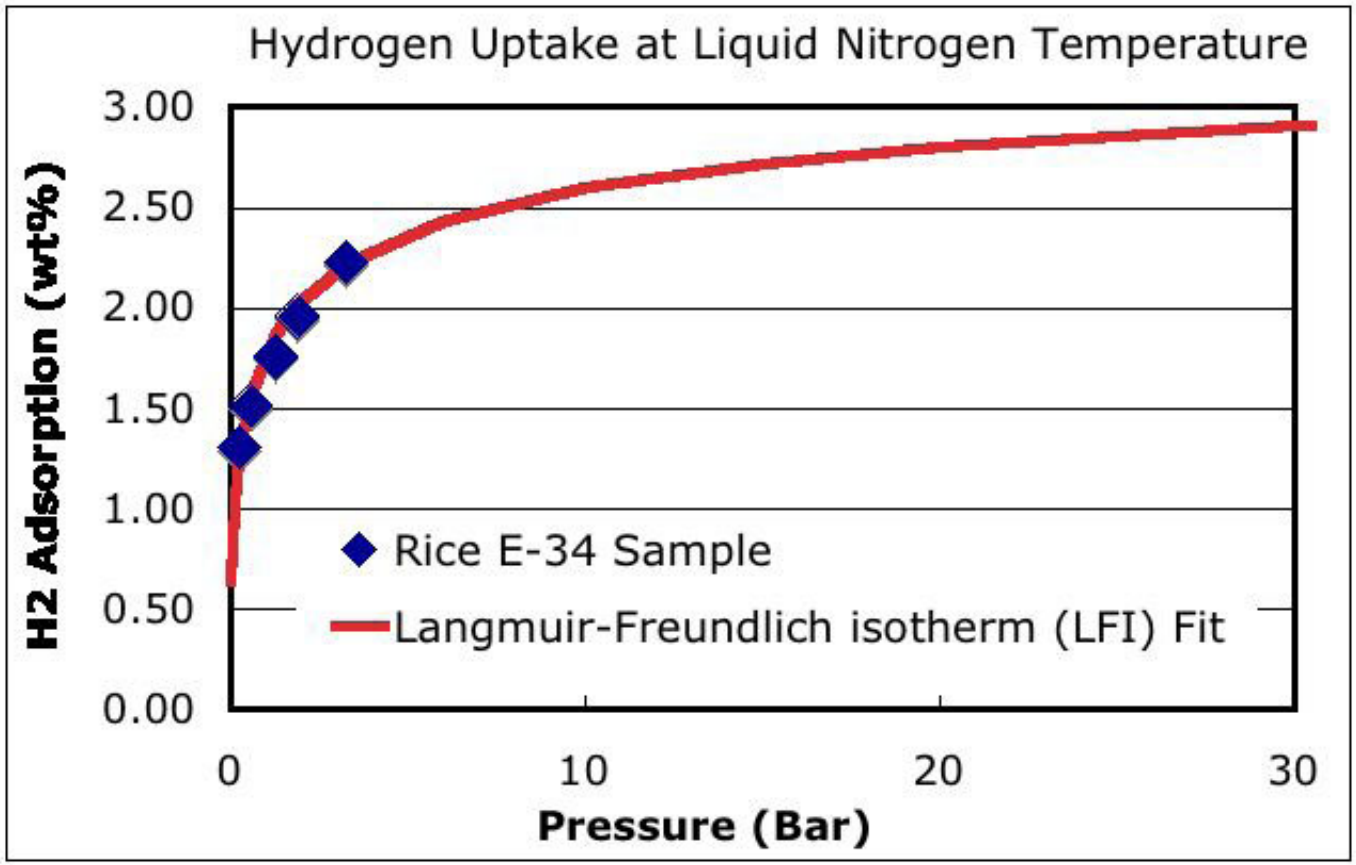
•The nanotube is cut, functionalized, attached to a metal catalyst, reductively docked to the end of the nanotube and grown with retention of its original diameter and symmetry.
•The metal catalyst dissociates the carbon feedstock and adds the carbon to the nanotube
•Catalyst is typically iron; in some cases cobalt and molybdenum maybe used

•**This provides an unlimited supply of identical nanotubes**

Technical Accomplishments

Hydrogen storage on ozone bulk processed SWNTs

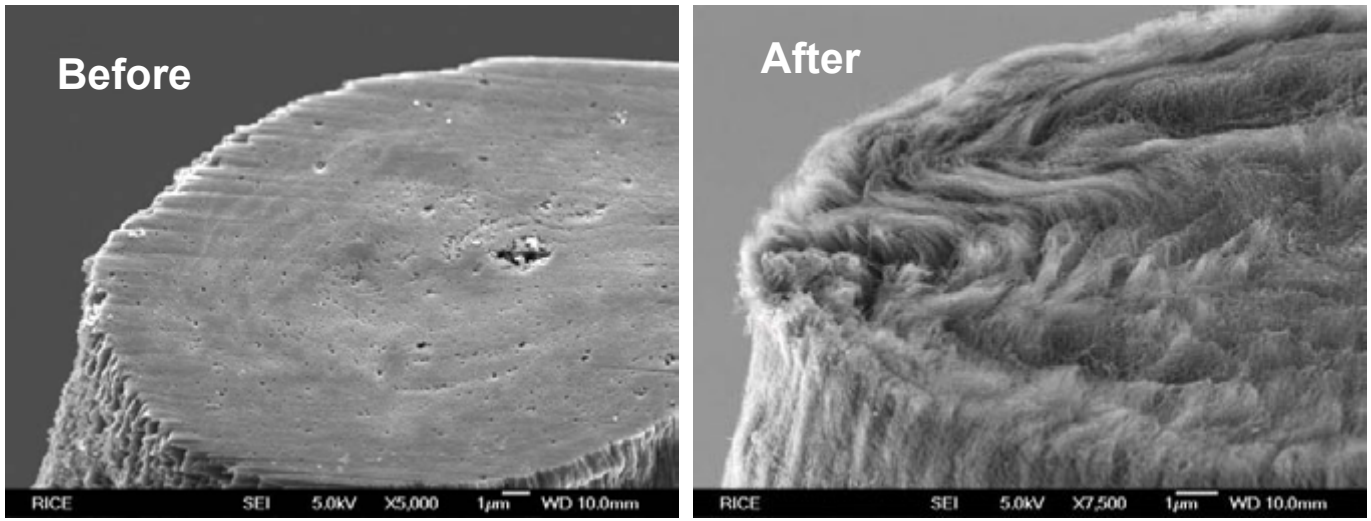
- **Ozone treated sample baked at 1000 ^{o}C to create pores; surface area is 1050 m^3/L**
- **Extrapolating to nanoengineered 3D structure: Uptake of 6.4 wt%**



SWNTs show excellent hydrogen uptake when pores are made available

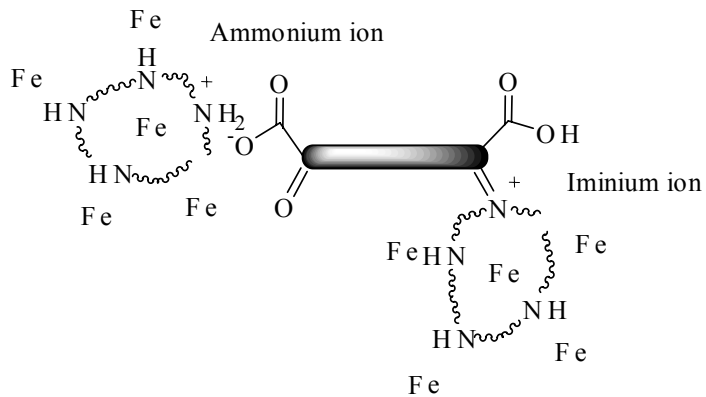
Technical Accomplishments

Cloning from the end of a SWNT fiber after evaporating metal catalyst onto the end
New growth proven to be identical tubes grown from the ends of original tubes.



Liquid phase docking of catalyst achieved, one of three successful docking methods is illustrated on the right.

Demonstration of cloning with the solution phase docked catalysts is in progress. Preliminary results indicate successful cloning.

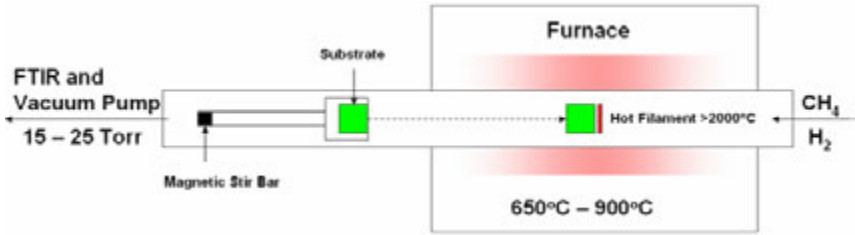


Sorting by type has been demonstrated

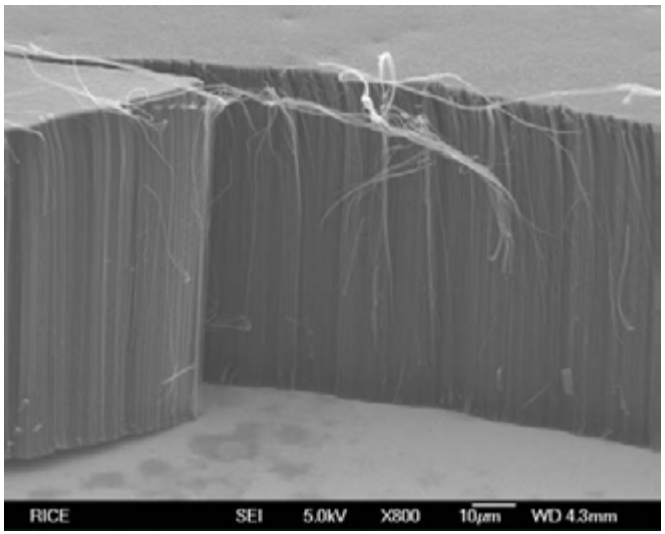
Cloning has been demonstrated, which will enable exact reproduction of specific types.

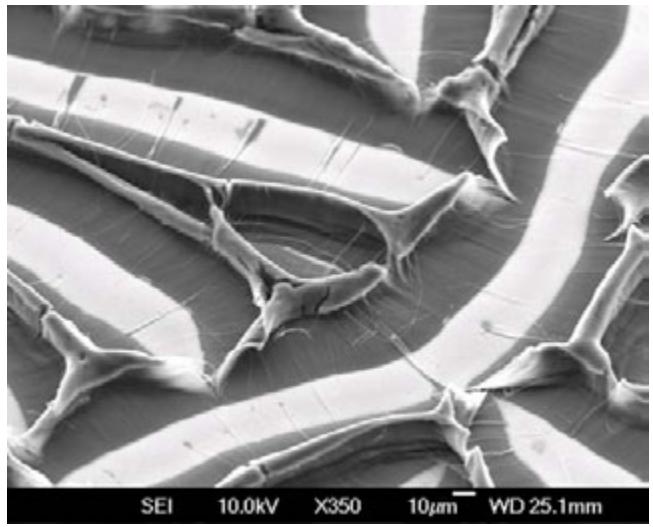
Technical Accomplishments

Vertically aligned SWNT carpet growth



Densification of VA-SWNT Carpets has been carried out mechanically and by a wetting and drying process (shown below) yielding a VA- carpet with up to 70% of maximum density.



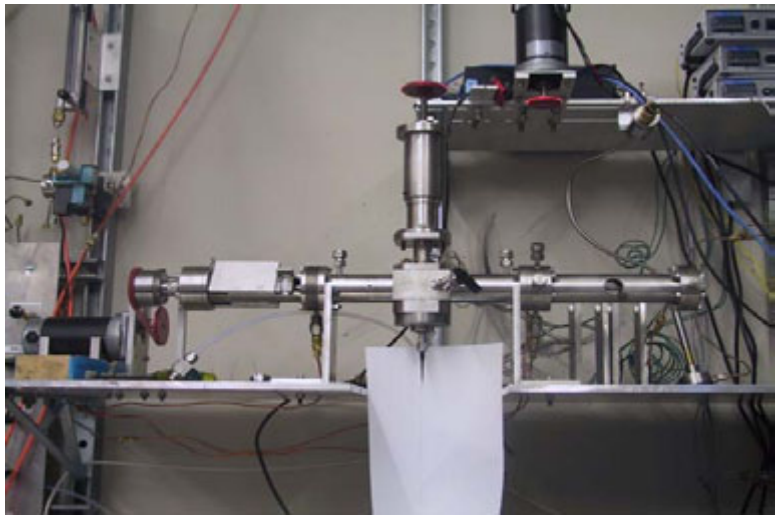


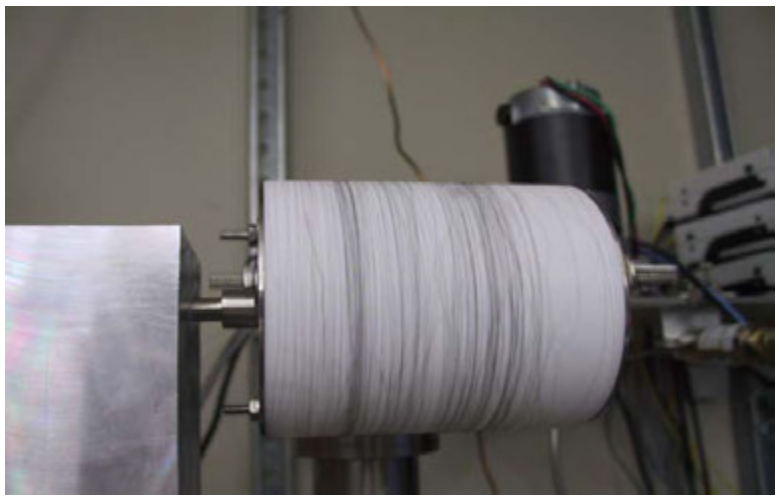
Hot filament CVD has been developed to grow vertically aligned arrays of all SWNTs that have a precise tube length and a narrow diameter range centered around 1 nm.
We have used other CVD methods to grow larger diameter VA-SWNT carpets.

Reproducible growth of easily densified SWNTs using inexpensive, rapid, and scalable processing enables construction of advanced hydrogen sorption materials

Technical Accomplishments

SWNT Fiber Spinning in Oleum

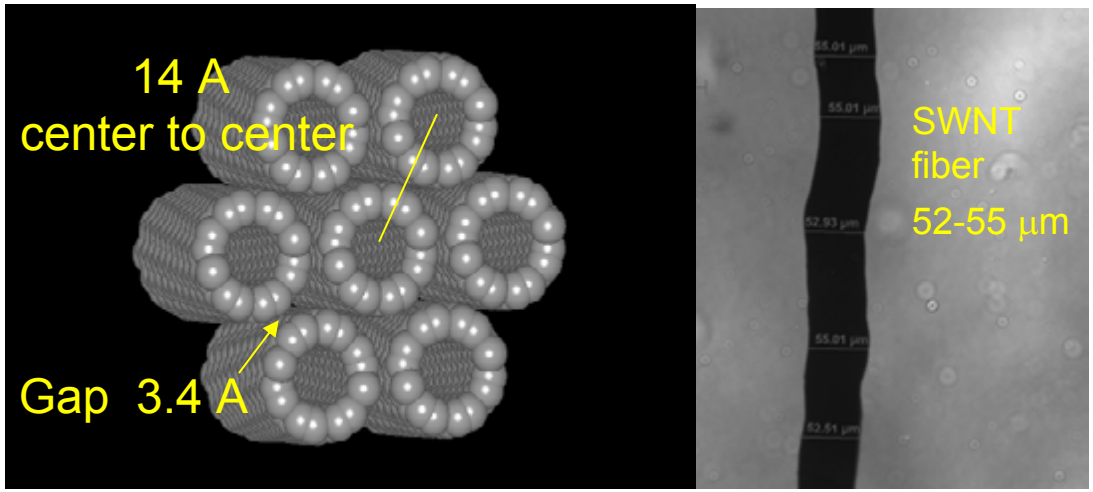




- Upper photo- **Laboratory engineered SWNT fiber spinning apparatus continuously extrudes 100% pure carbon fibers from an oleum suspension.**
- Lower photo- **Single continuous SWNT fiber wound up on the take up drum; single nozzle production: 2 g/hr.**

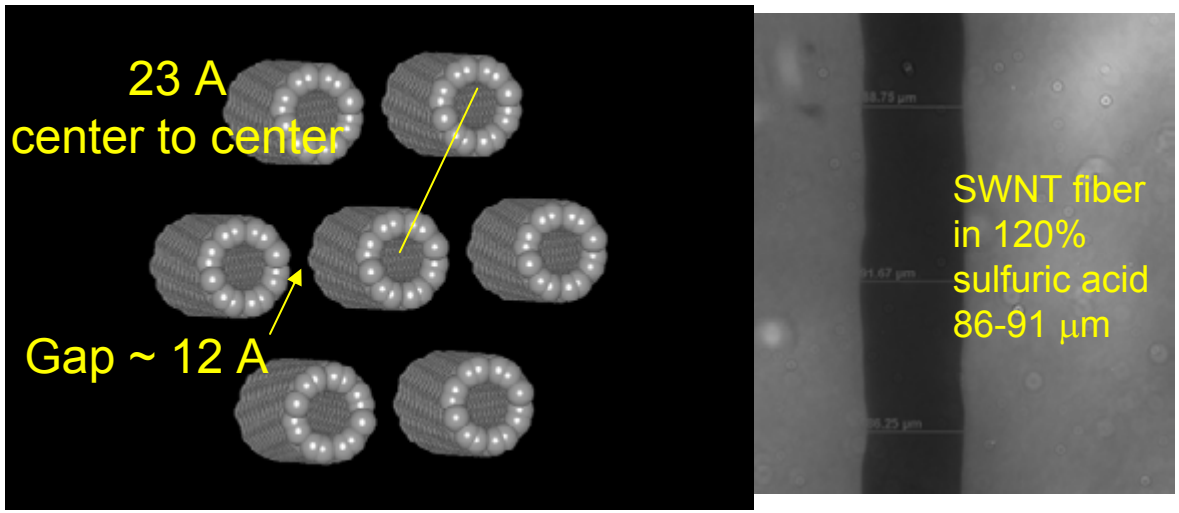
- **These fibers (75-80% maximum density) are the feed stock for swelling and cross linking to make the 3D nanoengineered structure**
- **SWNTs exhibit highly anisotropic transport, axial thermal conductivity quite superior to copper, essential for efficient heat removal.**
- **Can deliver the enthalpy of adsorption to a single (or two) end plate(s) of cylindrical tank.**
- **Uniaxial heat transport allows unlimited 2D scaling in transverse dimensions without increased fill time.**
- **SWNT fibers arrayed in parallel provide efficient non-torturous gas flow.**
- **This experiment shows that SWNT fibers for a non-granular storage media can be produced by conventional wet spinning techniques; fully scalable to mass production**

Technical Accomplishment



Expanded fiber

SWNT fiber bundle, as produced by spinning. Nanotubes are closely spaced due to van der Waals attractive forces.



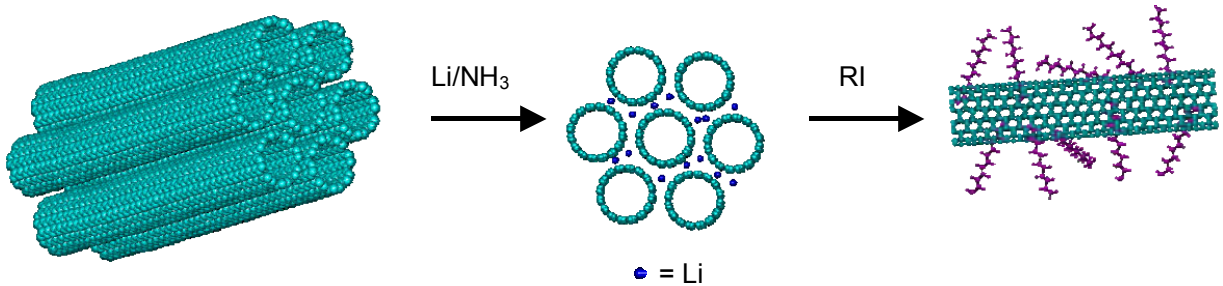
SWNT Bundle, swollen in 120% H_2SO_4. which increases the tube-tube spacing due to uniform coating of the acid that intercalates onto the walls of each SWNT

The data show that nanotube spacing in the fiber can be expanded as desired, with the scale of expansion dependent on the acid concentration. This expansion is locked into place with crosslinking

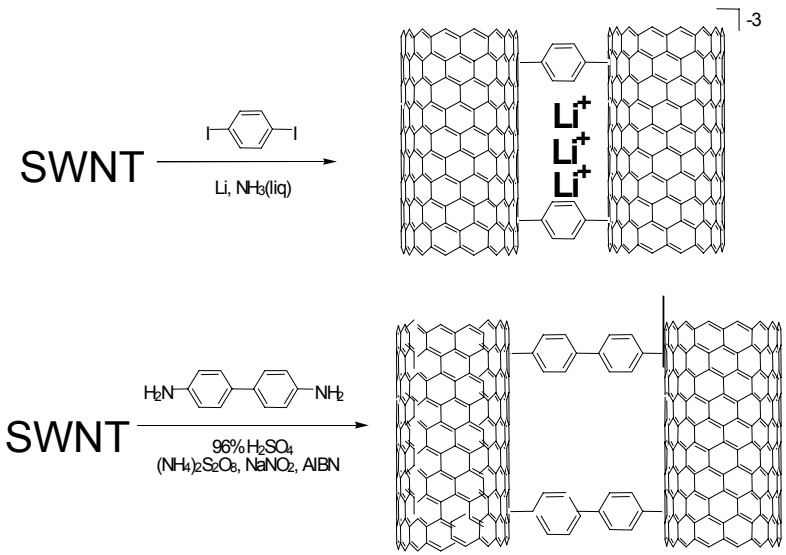
Technical Accomplishments

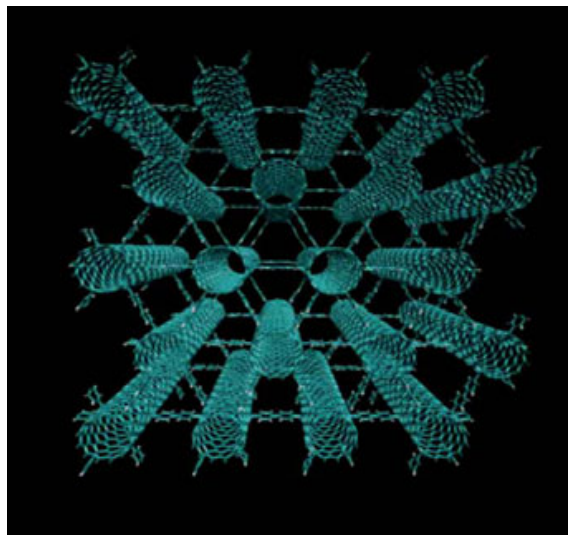
Conversion of Carpets or Fibers to 3D NanoEngineered Arrays

Lithium is proven to intercalate and is used to promote chemical binding



Oleum intercalation swells nanotube bundles then derivatives are used to crosslink the expanded bundles into arrays





SWNT spacing is nanoengineered to make ~100% surface area available for H_2 storage
Only nanoengineering can provide a specific and uniform pore size in the carbon .

Technical Accomplishments

Insight from Density Functional Theory

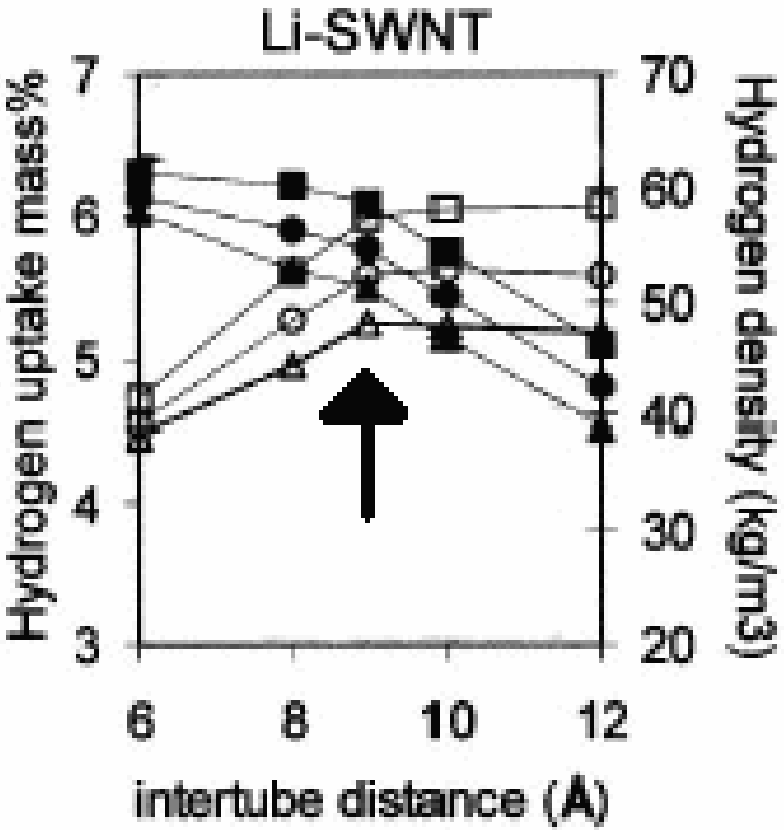


Figure adapted from: Deng, Wei-Qiao; Xu, Xin; Goddard, William A. *Phys. Rev. Lett.* **2004**, 92, 166103

- **Hydrogen uptake for lithium doped SWNTs at room temp; a function of pore size**
- **Simultaneously addresses both weight (left) and volume (right).**
- **White squares are mass% and black squares are density.**

- **There is a specific pore size that is optimum when mass and density are both considered.**
- **This crossover occurs at 9 Angstroms (arrow)**
- **This remains ~constant over a wide range of pressures (10, 20 and 50 atm shown)**

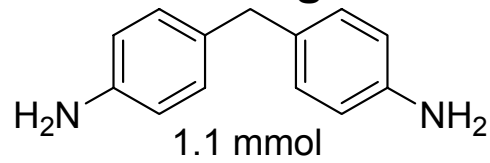
- **For SWNTs without lithium, the crossover point may dictate a different pore size.**
- **Rice Colleague Boris Yakobson has recently added effects entropy, indicates increased H2 capacity for larger pores**

The most important lesson from the theory:

There exists an ideal pore size, and all pores should be this uniform size.

Technical Accomplishments

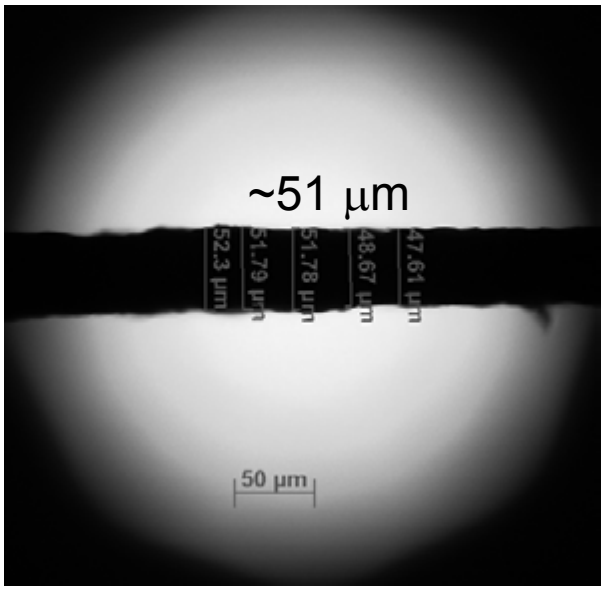
Swelling and Crosslinking of SWNT Fiber in Oleum



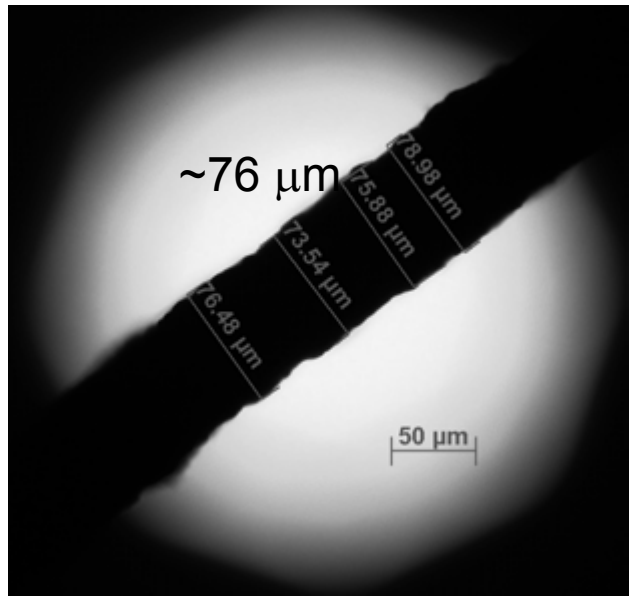
SWNT Fiber
No mounting

$NaNO_2$
AIBN
Oleum (120%)

Crosslinked Fiber



Pristine Fiber



Crosslinked Fiber

Crosslinked swollen fiber exhibits a 50% increase in diameter; corresponds to a 9 A pore
The spun fiber remains intact after the pore expansion process and drying.
The nanoengineered medium is a self-supporting, readily handled macroscopic object.

Next step: Make and test several specific pore sizes for optimum hydrogen uptake.

Future Work-2006

FY2006

Measure H2 uptake by new 3D nanoengineered structures (June 06)
Develop methods for varying the 3D spacing of the nanoframe (July 06)
Begin (parametric) studies of pore size vs. hydrogen uptake (August 06)
Adapt 3D nanoengineering methodology to carpet grown fibers (July 06)

Milestone >4 mass% uptake (August 06)
Milestone >30 g/L uptake (Sept 06)

Develop type selection methods with 90% selectivity by type (August 06):
Decision point—select the best nanotube type(s) (August 06)
Develop catalyst methods for uniform carpet growth, narrow range of diameters and types (Sept 06)
Decision point– choose the best method for adjustable pore spacing (Sept 06)

Future work-FY2007

- Test **pore spacings** in the range of 0.8 to 1.8 nm intertube distance (Oct 06)
- Apply cloning methods to chirality selected individually identifiable nanotubes (Nov 06)
- **Decision point**: Select optimum nanoengineered pore size (Dec 06)
- Develop reproducible carpet growth densification to 70±10% (Jan 07)
- Develop Li:SWNT intercalation methodology for room temp. uptake (Feb 07)
- **Decision point:** Select optimum fiber spinning and carpet growth methods (Mar 07)
- **Milestone** for Li:SWNT: 4 mass% uptake (Apr 07)
- **Decision point**: Select best lithium intercalation method (Apr 07)
- Quality test for reproducible cycling, goal of 90% capacity retention after 20 cycles. (May 07)
- **Milestone**: H2 uptake in pure carbon nanotubes with 3D nanoengineered pore size at 77K, uptake 6wt% and 45 g/L (July 07); 2x greater than 2006, and 4x greater than 2005
- Scale up fiber production to 10,000 meters (approx. 100 grams) by Sept 07
- Scale up carpet production to 10,000 square cm (approx.10 grams) by Sept 07
- **Milestone** for Li:SWNT: uptake 6wt% and 45 g/L (Sept. 07)
- **Milestone for pore size**: Determine tolerances for uniformity of pore size, adverse impacts of oversize/undersize pores for both mass and volume considerations (Sept 07).

Summary

- Developed processing steps required for cloning SWNT
- Formulated nanopore engineering concept for construction of optimum pore size in dense SWNT solids for H_2 storage.
- Uptake in expanded surface area processed SWNTs extrapolates to 2.9 wt%
- Reliable pure SWNT fiber spinning developed
- Vertically aligned SWNT carpet growth developed

Cloning SWNT

Cutting single wall carbon nanotubes (Three cutting methods developed)
Sorting single wall carbon nanotubes (Sorting by length and type developed)
Preparation of cut tubes with metal catalyst (Developed for iron catalysts)
Growth of seeds on supports (Demonstrated growth on supports)

Nanopore Engineering (precise control over SWNT pore structure)

Opening of tube ends (done)
Tube length (done– shown here)
Tube type (n,m) (en route– shown here)
Formation of dense 3D arrays (shown here)
Fix inter-nanotube spacing in arrays with 50% expansion and crosslinking
corresponds to 9 Angstrom pore spacing (shown here)
Efficient Li insertion into the 3D arrays (en route– shown here)

Summary Table

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY05 materials****	**FY06 Result materials****
Specific Energy	kWh/kg (wt. % H2)	**2.0 (6 wt%)**	**0.43 1.3 wt%**	**0.97 2.9 wt%**
Volumetric Energy Capacity)	kWh/L	**1.5**	**0.43**	**0.97**
Desorption Temperature?			>77K	>77K
Plateau Pressure			Measured at 2 bar	Fit to 30 bar

Supplemental slides

- End of presentation

- Supplemental slides follow

Critical Assumptions and Issues-1

- **Assumption for rapid filling: The heat of adsorption must be quickly removed**
- SWNTs have been proven to have uniaxial thermal conductivity considerably better than copper, approaching that of diamond (>15 W/cm-K)
- Non-granular aligned fibrous media transports enthalpy of adsorption to a specific location for heat removal
- **Assumption for fully utilized capacity: Uniformity of binding energy is needed**
- Nanoengineered structures are assembled from molecules all alike
- "Mysteries" of binding disappear
- In contrast, processing bulk materials will inherently lead to variability in binding sites
- **Assumption for maximum capacity: Regular spacing of binding sites**
- Nanoengineering will make any good material better.
- Binding sites will always have better packing and hence more capacity than irregular sites.
- All surfaces are accessible.
- **Assumption for minimum volume: Uniform spacing of structural components is required**
- Nanoengineering is essential to avoid dead volumes due to spaces that are too large or too small.

Critical Assumptions and Issues-2

- **Assumption for maximum cycle life: Physisorption does not alter chemical structure**
- Physical adsorption of hydrogen does not alter size, shape, or chemical structure, so it will cycle indefinitely. There is no forced intercalation.
- Contaminants of 100 ppm water/50 ppm oxygen in the hydrogen will deactivate less that 10% of the lithium in 200,000 miles of driving.
- **Assumption for physisorption at room temperature: Metal greatly enhances uptake**
- The Li:SWNT uses the lightest metal for the lowest mass per molecule
- Lithium becomes charged because SWNTs can accept N-doping
- Raises H2 binding energy to ~10 kcal/mole,
- Well above the minimum ~7 kcal/mole needed for RT binding.
- **Assumption for ultimate low cost: Avoid use of precious metal catalysts**
- The nanotube storage tank media is constructed entirely of abundant light elements
- **Assumption for gas transport: A linear path is more efficient than a tortuous path**
- Straight line transport paths in nanoscale 3D space frame
- Straight line transport paths in macroscale regular fiber array

Critical Assumptions and Issues-3-Cost

- Projected costs:
- SWNTs are presently available in bulk quantities for about $1000/kg, compared to$1000/g ~7 years ago, decreasing ~one order of magnitude every 3 years.
- Feedstock is CO or methane which are some of the lowest cost sources of carbon. The catalyst is iron.
- Trendlines indicate a cost of dollars to tens of dollars per kg in a few years, and undoubtedly will be driven down by demand.
- Sulfuric acid (oleum) and analine compounds needed to nanoengineer the pore size are inexpensive, and will add ca. 20% to the cost.
- The spinning process to make the spun carbon nanofiber media is completely scalable, and is essentially the same wet spinning process used in making millions of pounds of Kevlar, Zylon, acid-spun nylon, etc.
- Spinning is fully scalable, and costs are expected to be tens of cents per pound or less.

Publication List

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6. Price, B. K.; Hudson, J. L.; Tour, J. M. “Green Chemical Functionalization of Single Walled Carbon Nanotubes in Ionic Liquids,” *J. Am. Chem Soc.* 2005, *127*, 14867-14870.
7. Dyke, C. A.; Stewart, M. P.; Tour, J. M. “Separation Of Single-walled Carbon Nanotubes On Silica Gel. Materials Morphology And Raman Excitation Wavelength Affect Data Interpretation,” *J. Am. Chem. Soc.* 2005, *127*, 4497-4509.
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9. Ericson, Lars M., et.al., “Macroscopic, Neat, Single-walled Carbon Nanotube Fibers”, *Science*, 2004, *305*, 1447-1450