Nanoscale Materials for Human Space Exploration: Regenerable CO_2 Removal

NanoMaterials Project
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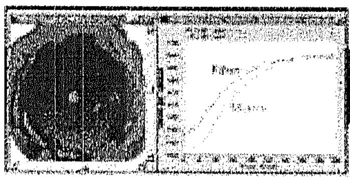
Nanomaterials: Fundamentals to Applications

Growth/Production
Laser and HiPco
Production and
Diagnostics

Characterization
Purity, Dispersion, Consistency, Type
SWCNT Load Transfer
Single Fiber Diffusivity

Processing
Purification
Functionalization
Dispersion
Alignment

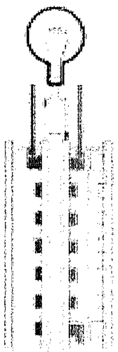
Collaboration
Academia, Industry, Government



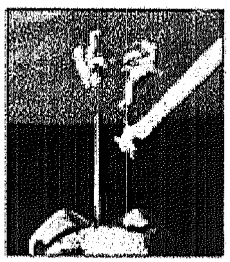
Single Fiber Thermal Diffusivity

Applications For Human Spaceflight

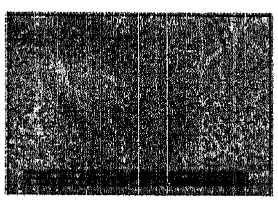
APPLICATION	PARTNERS	TRL 1	2	3	4	5
Ultracapacitors	EP, Glenn, Industry	X	X	X	X	
Proton Exchange Membrane – PEM - Fuel Cells	EP, Glenn, Industry	X	X			
RCRS - Regenerable CO_2 Removal System	EC, Ames, Industry	X	X			
Active / Passive Thermal Management Materials	EC, Rice, ORNL, Industry	X	X			
Nanofiltration for Water Recovery	EC, Industry	X	X			
Electromagnetic Shielding Materials (ESD/EMI)	EV, Rice, LaRC, Industry	X	X	X		
Advanced Nanostructured Materials for Thermal Protection and Control	ES3, Ames, Goddard, Industry	X	X			
Radiation Dosimeter	NX, Rice, PV, LaRC, Ames	X				
Nanotube-Based Structural Composites	ES, Rice, UH, LaRC	X	X			



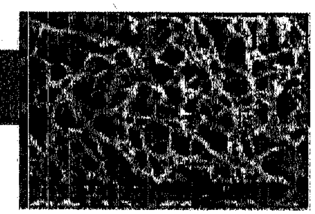
Fuel Cells



Ultracapacitors (SAFER)



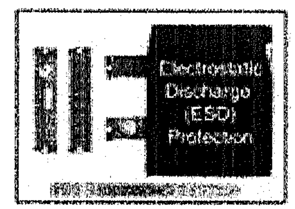
Nanofiltration



Ceramic Nanofibers (TPS)

High Thermal Conductivity Fabrics

CO_2 Removal

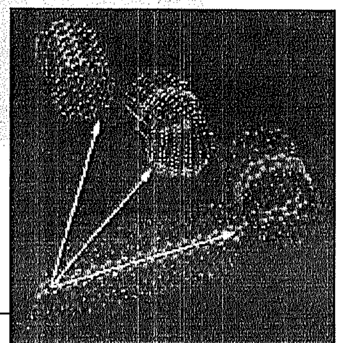


Electromagnetic Shielding

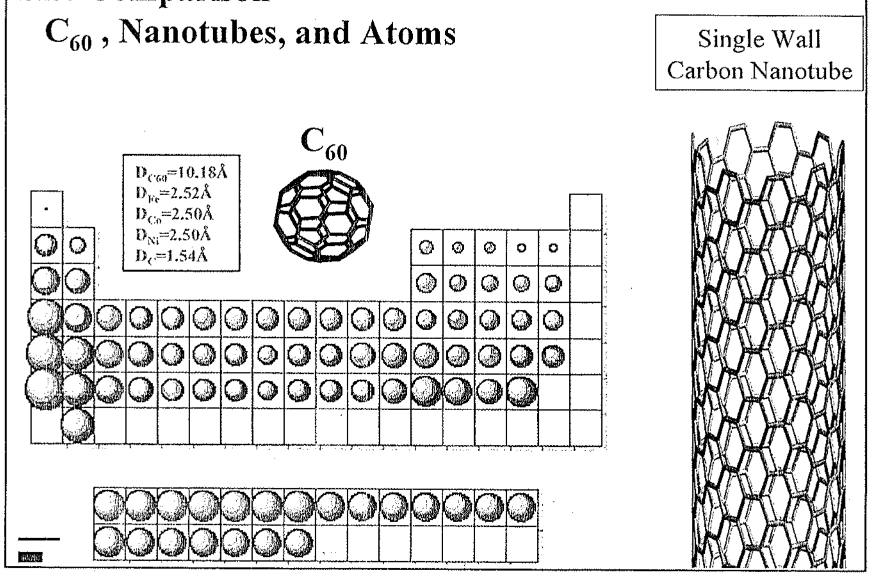
Nanomaterials: Single Wall Carbon Nanotubes

Unique Properties

- Exceptional strength
- Interesting electrical properties (metallic, semi-conducting, semi-metal)
- High thermal conductivity
- Large aspect ratios
- Large surface areas



Size Comparison –
C_{60}, Nanotubes, and Atoms



Possible Applications

- High-strength, light-weight fibers and composites
- Nano-electronics, sensors, and field emission displays
- Radiation shielding and monitoring
- Fuel cells, energy storage, capacitors
- Biotechnology
- Advanced life support materials
- Electromagnetic shielding and electrostatic discharge materials
- Multifunctional materials
- Thermal management materials

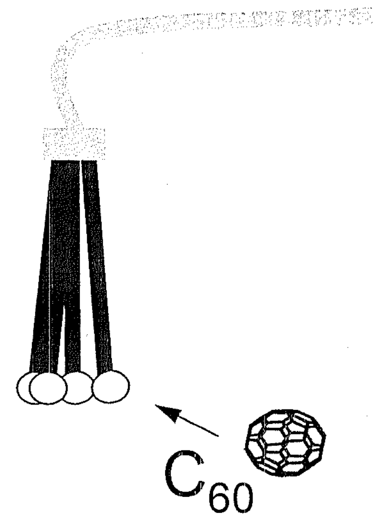
Current Limitations

- High cost for bulk production
- Inability to produce high quality, pure, type specific SWCNTs
- Variations in material from batch to batch
- Growth mechanisms not thoroughly understood
- Characterization tools, techniques and protocols not well developed

NASA JSC Nanomaterials: Environmental Applications

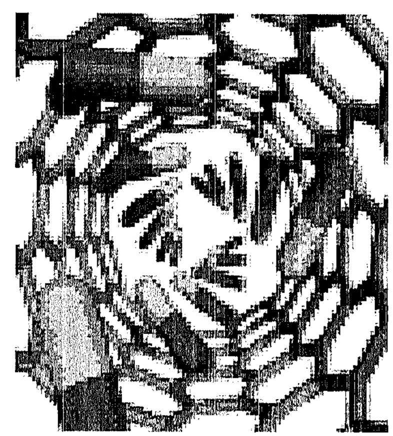
Water Purification

- NASA JSC Structural Engineering and Crew & Thermal Systems Divisions
- Use light induced production of singlet oxygen by fullerenes to destroy harmful microbes in water supplies
- Developing process for attaching fullerenes to fiber optic cables
- CDDF 2005 – Report December 2005



Alcohol Removal System

- NASA JSC Structural Engineering & Biomedical Systems Divisions
- Use aligned carbon nanotubes to separate alcohol from water supplies
- Testing various membranes
  - Phase 1. Buckypaper type materials
  - Phase 2. Vertically aligned MWCNT in a matrix
- CDDF 2005 – Report December 2005



Air Revitalization: some current technologies

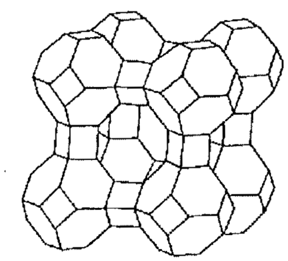
Lithium Hydroxide: Not suited for long duration missions since it is non regenerable

$$2\,LiOH \cdot H_2O(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + 3\,H_2O(g)$$

$$\Delta H^\circ = +\,3.8\ \text{kcal/mol LiOH},$$

Zeolite 5A that physisorbs CO_2

- Requires 200C to renew the adsorbent – high power consumption
- Lower surface area to volume ratio



MetOx – Metal Oxide (AgO) reacts with CO_2 to form a carbonate.

- Large system mass – not optimal for PLSS
- Also requires high temperature

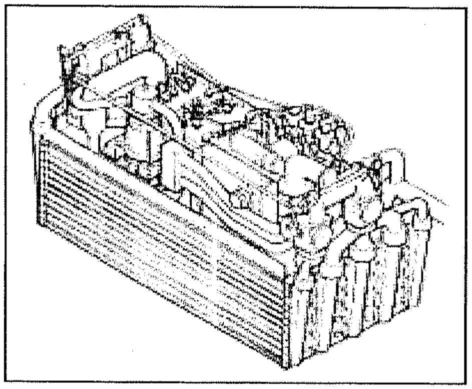
$$Ag_2O + CO_2 \xrightarrow{H_2O} Ag_2CO_3$$

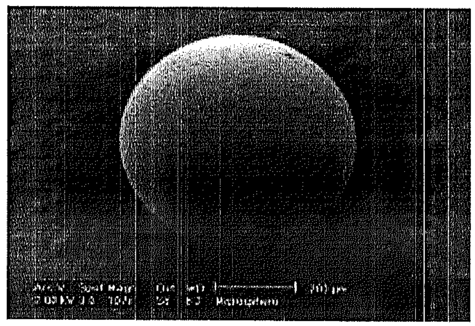
$$Ag_2CO_3 \xrightarrow[220C]{\Delta} Ag_2O + CO_2$$

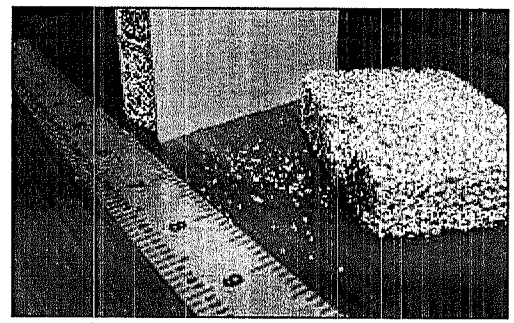
Supported Amines for Air Revitalization

Advanced solid amine bed system flown in mid-1990's (pressure swing)
- Volume constraints, thermally inefficient, amine volatility
- Not suited for planetary use (need temperature swing)
- Surface area ~100 m^2/g

Need for new material: high surface area, high thermal conductivity, ability to be coated with amine system





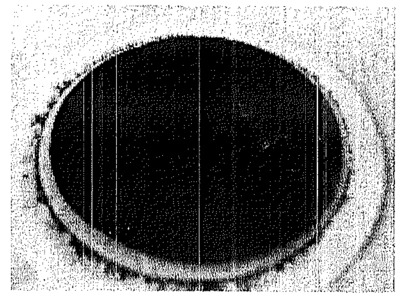


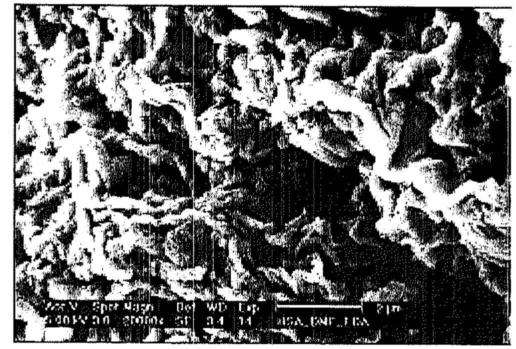
Polymer Bead **and** Aluminum Structure

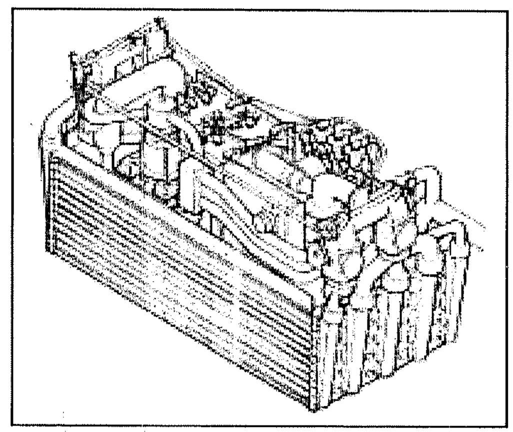
Carbon nanotubes may offer a thermally conductive high surface area light weight support material for this application

Initial Results and Technology Assessment

- Carbon Nanotubes have high surface area: bucky pearls, fibers, bucky paper
- TGA experiment: the amine is reactive with the CO_2 gas stream
- Poor adherence to nanotube surface - requires a specific pore size and shape
- We need a better way to integrate the support phase with the amine

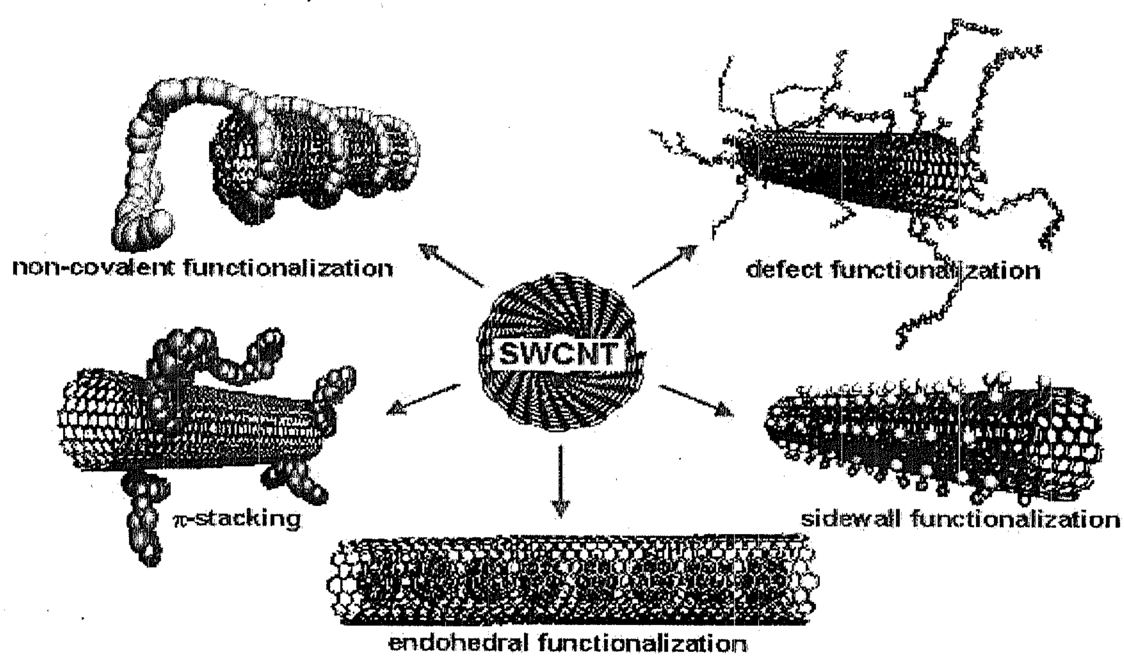






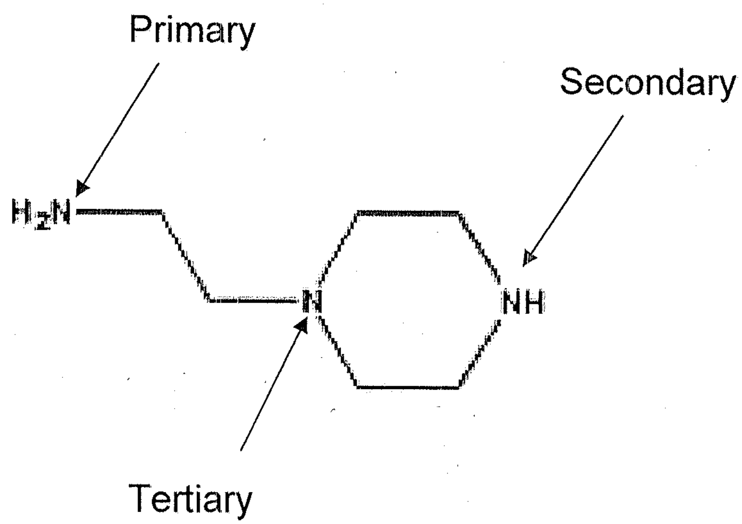
Functionalization of SWCNTs with amine groups

- Since amines are volatile the coating would be prone to degradation during repeated thermal or vacuum driven renewal of the adsorbent.
- Chemically bonding of the amine to the support phase was a solution to this problem



Functionalization of SWCNTs with amine groups

- Collaboration with Dr. W. E. Billups group and Dr. J. Tour group (Rice University)
- Collaboration with Dr. T. Filburn (University of Hartford) to determine the types of amines that would be suitable for spaceflight needs



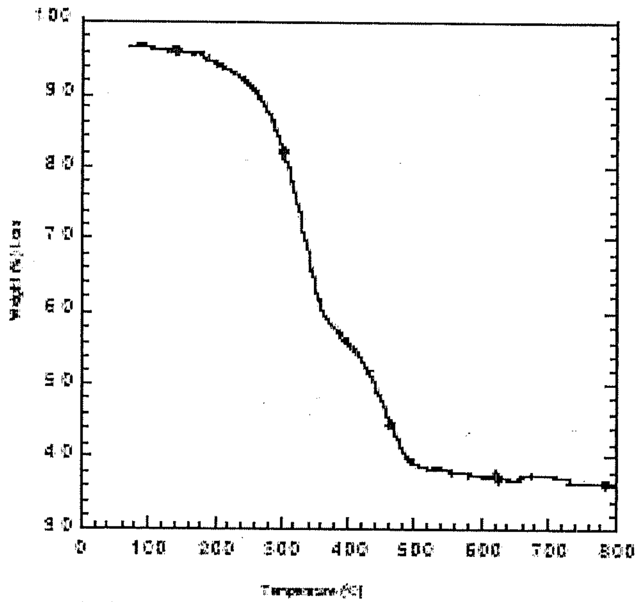
N-aminoethylpiperazine

Depending on their bonding amines have varying degrees of affinity for CO_2 capture and desorption

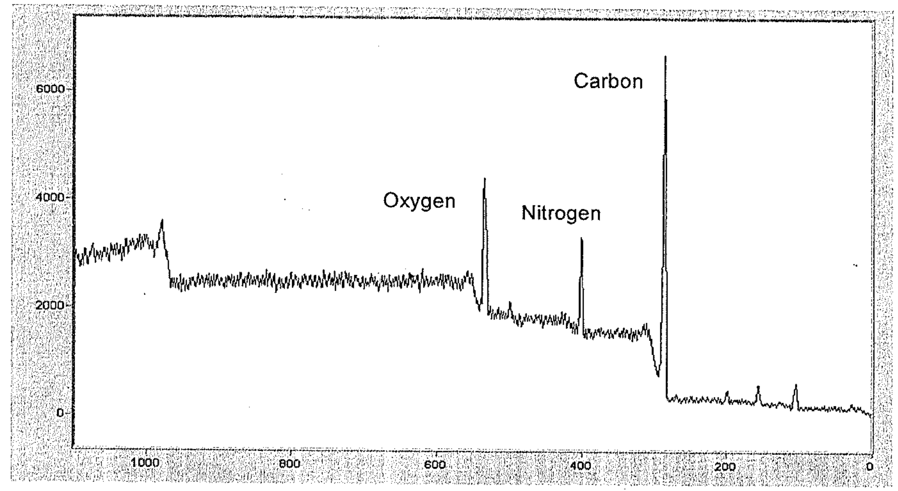
Primary binds CO_2 tightly, thus inhibiting desorption while tertiary amines bind CO_2 poorly

Secondary amines are preferred for pressure swing

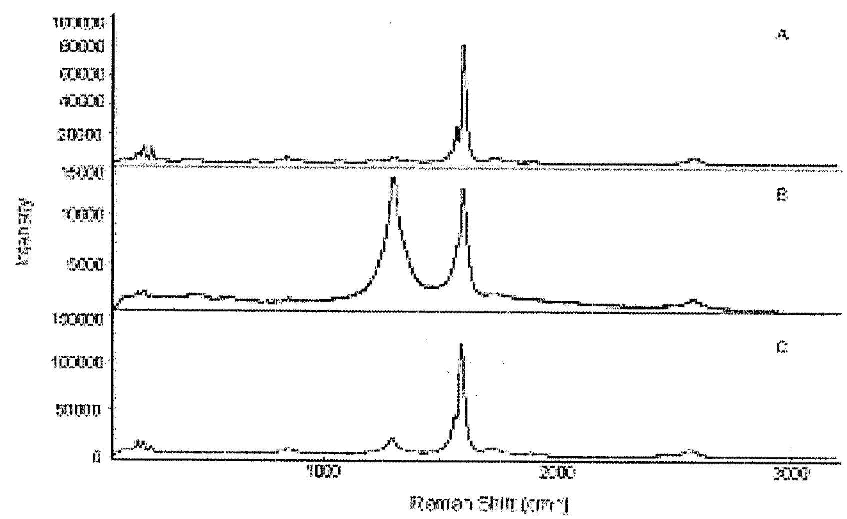
Characterization of Functionalized SWCNTs



TGA for PEI functionalized SWCNTS



XPS Spectrum of L-PEI functionalized SWCNTS

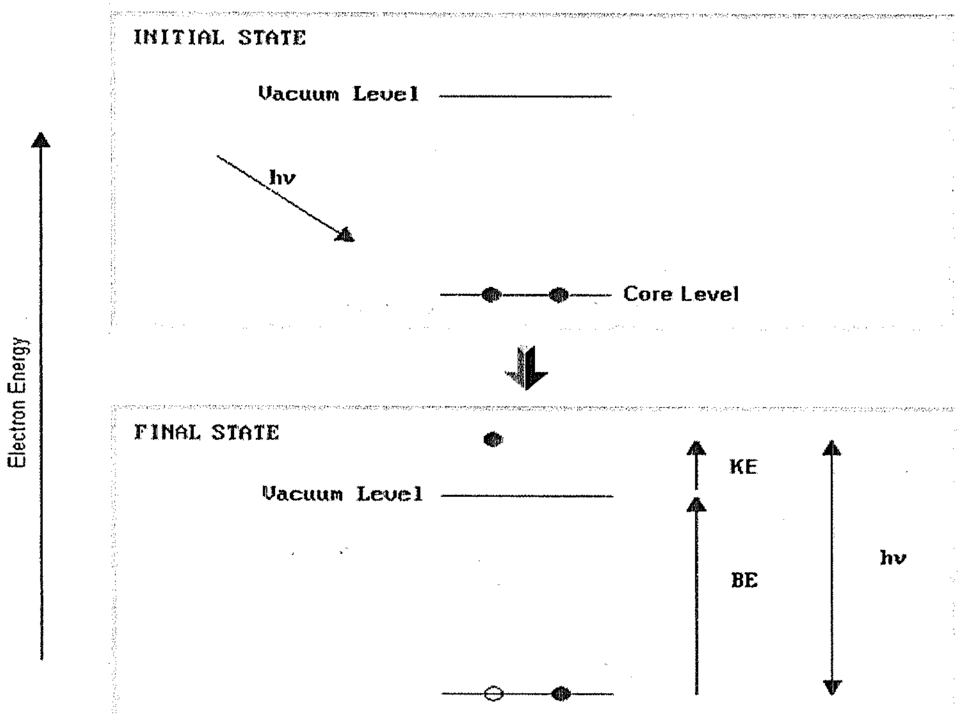


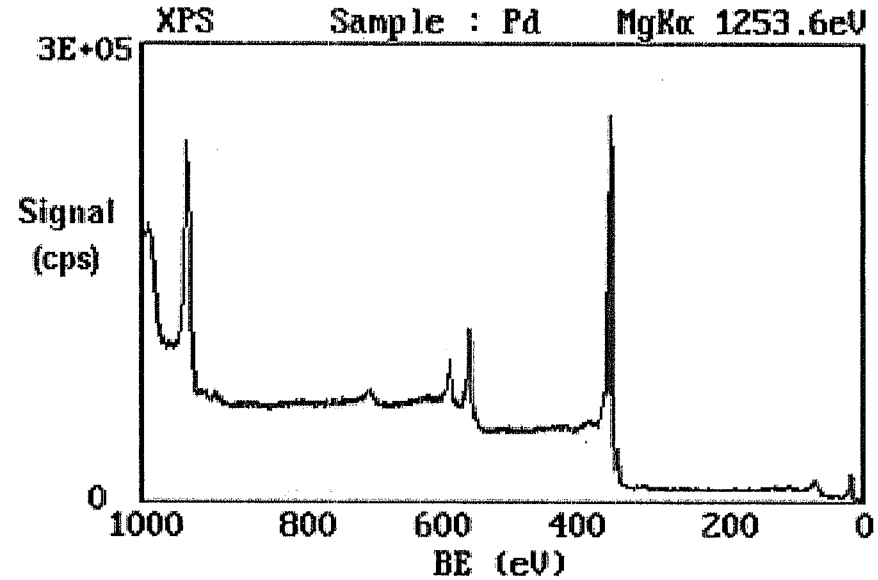
Raman Spectrum (780 nm) of:
a) Purified SWCNTS b) Dodecylated SWCNTS as synthesized c) Dodecylated SWCNTS after heating – the groups have been removed

Fundamentals of X-ray Photoelectron Spectroscopy (XPS)

<u>Single photon in/out process</u>

$$A + h\nu \rightarrow A^+ + e^- \quad (1)$$
$$E(A) + h\nu = E(A^+) + E(e^-) \quad (2)$$
$$E(A^+) - E(A) = BE \quad (3)$$
$$KE = h\nu - BE \quad (4)$$





Surface Technique

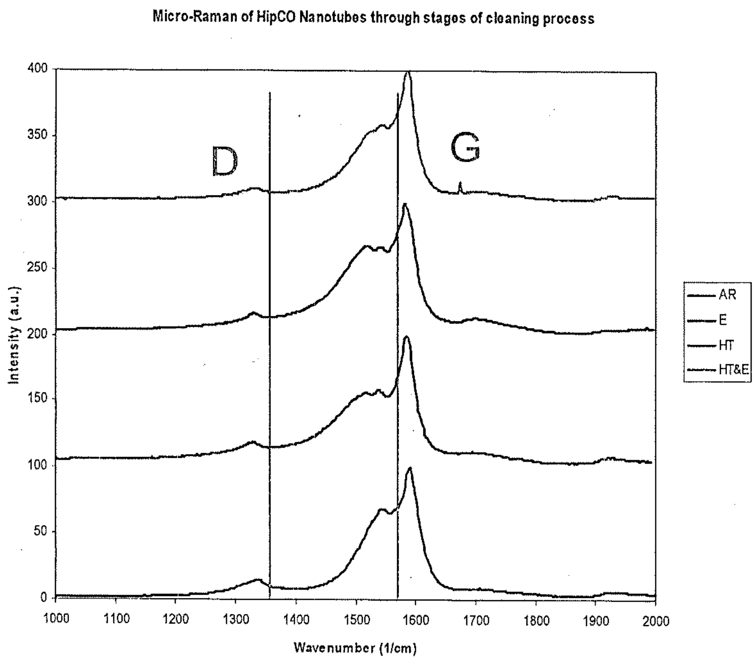
BE is unique for each element (ID)

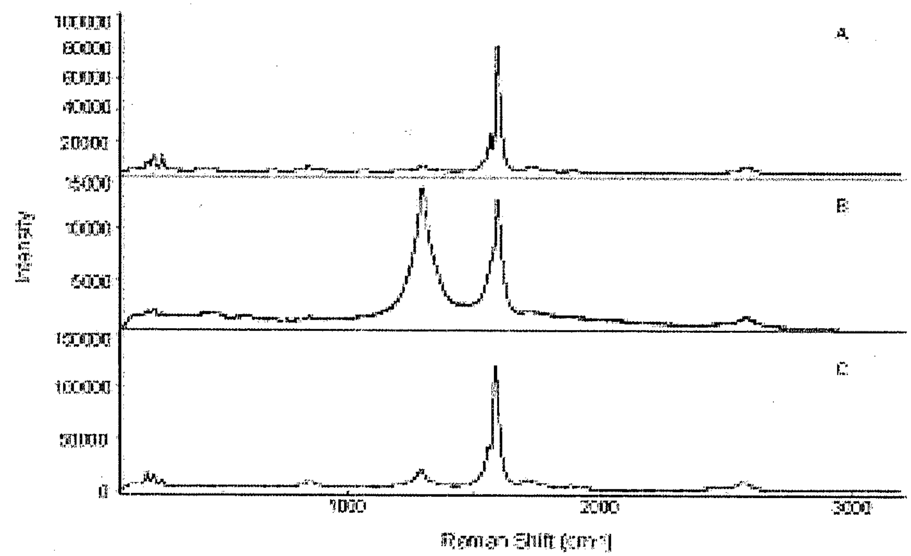
Calibration standards can be used to relate peak intensity to concentration

In collaboration with Rice University

Degree of functionalization via Raman Spectroscopy

A laser of varying wavelength is directed at the specimen and a small number of photons are inelastically scattered. The resultant change in energy between the incident and scattered photons allows one to determine the hybridization present between neighboring carbons





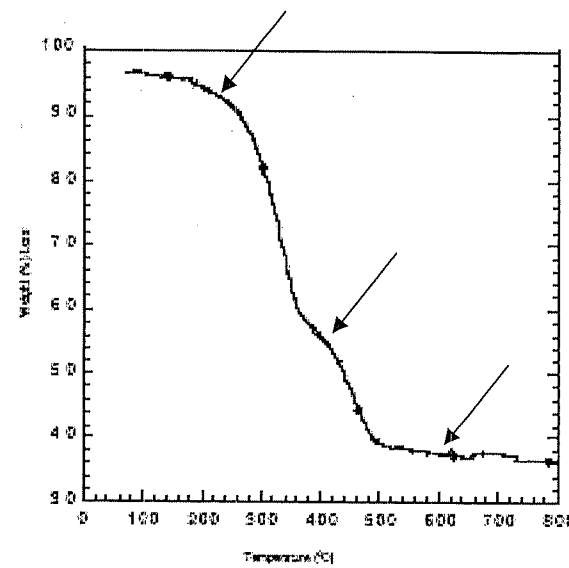
G peak indicates graphitic carbon, including SWCNT while D peak indicates disordered carbon

For functionalization, a larger D band peak indicates more groups have been attached to the nanotubes

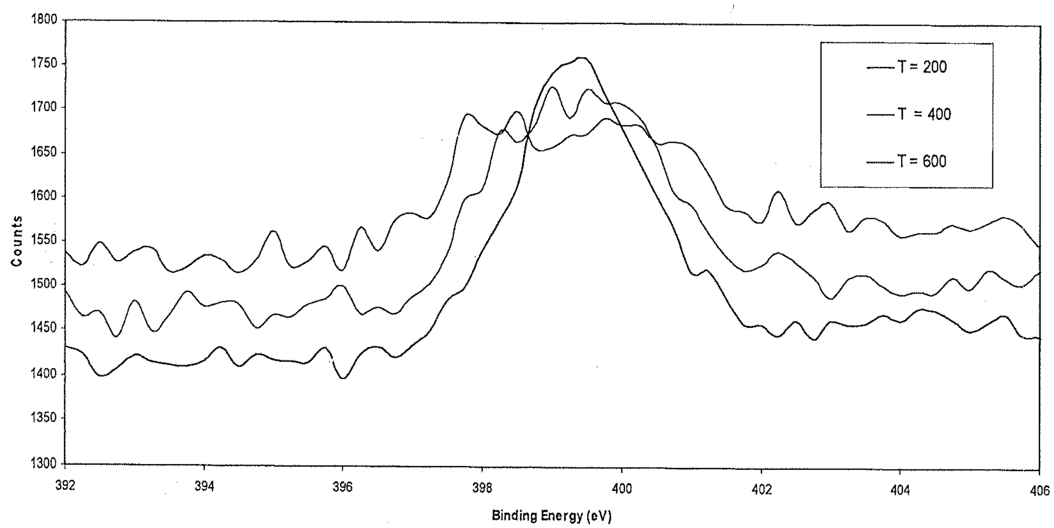
TGA/XPS Study of the Thermal Stability of Functionalized SWCNTs

TGA/XPS study of removal of functional groups

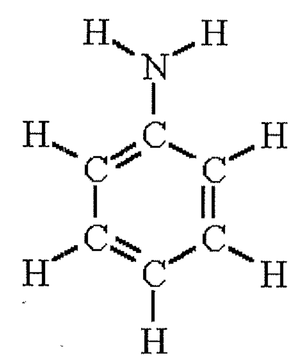
- Heat samples to various temperature and observe weight loss
- Examine XPS peaks characteristic of groups of interest
- Correlate weight loss to loss of functional group



TGA Weight Loss



XPS Data Spectra at 200C,400C and 600C



Aniline

Our results: The argument for functionalization

- Amenable to repeated cycling
  - Materials are thermally stable up to 100 C. (Thermal desorption takes place at 50 – 60C)
  - Chemical bonding of the amine to the support ensures these materials will be amenable to repeated vacuum desorption
- We have the tools and capability to manufacture materials
  - Collaborators at Rice (Tour and Billups) are experts in the area of nanotube functionalization
  - Chemistry is repeatable and reliable.
  - High amine loadings are possible especially with long branched amine polymers

Summary

- Presented background and review work on Regenerable CO_2 removal for spaceflight application
- Demonstrated new strategy for developing solid-supported amine adsorbents based on carbon nanotube materials

Acknowledgements

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- Dr T. Filburn (University at Hartford)
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