
Nanomaterials for space exploration applications
NanoMaterials Group
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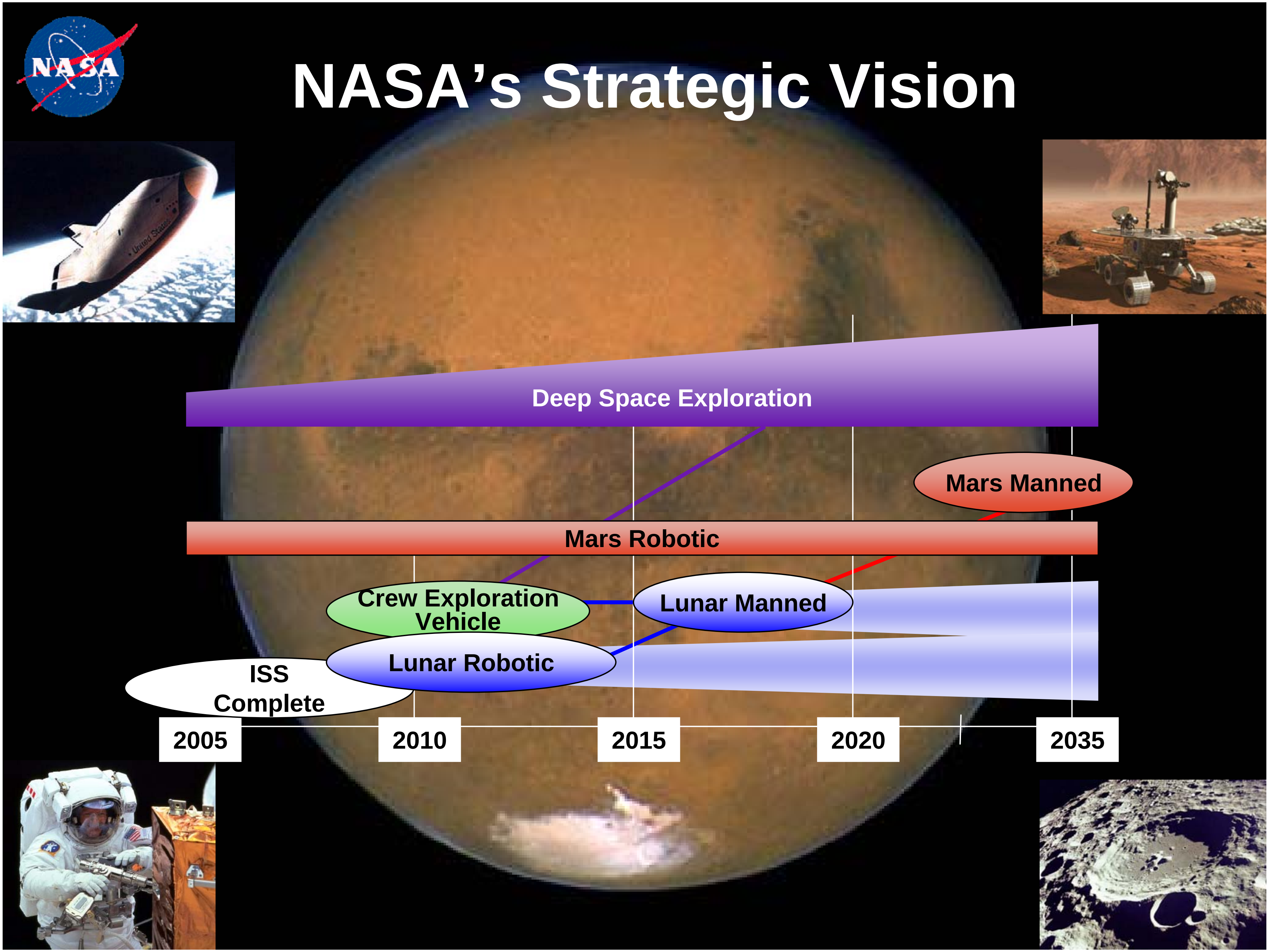
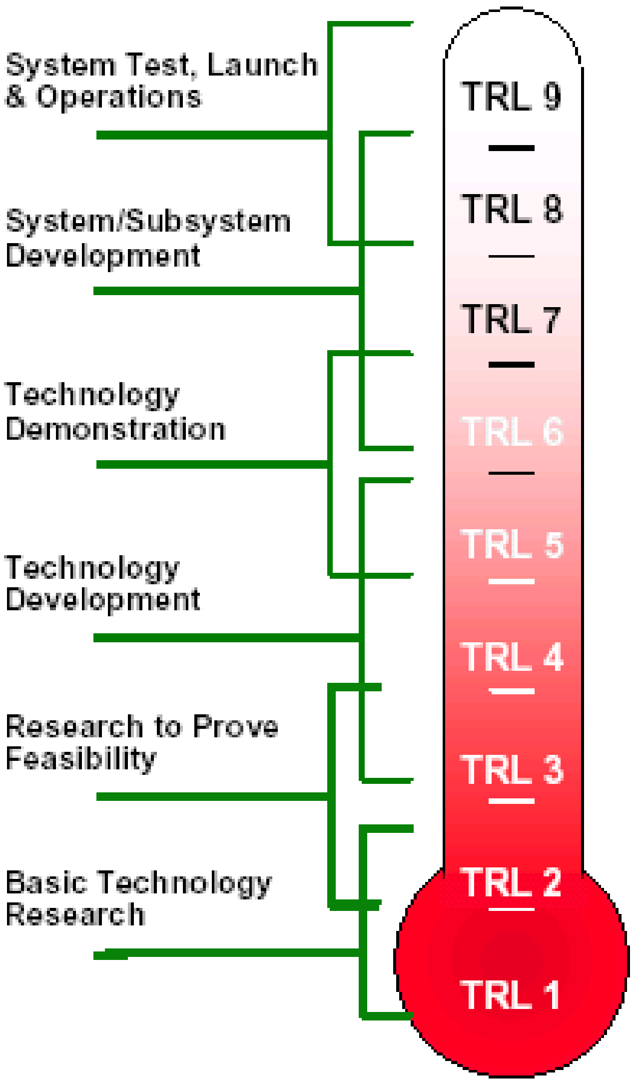
ENGINEERING
NASA
JSC


NASA
NASA's Strategic Vision
Deep Space Exploration
Mars Manned
Mars Robotic
Crew Exploration Vehicle
Lunar Manned
Lunar Robotic
ISS Complete
2005
2010
2015
2020
2035

Technology Readiness Levels (TRL)



- Actual system “flight proven” through successful mission operations
- Actual system completed and “flight qualified” through test and demonstration (Ground or Flight)
- System prototype demonstration in a space environment
- System/subsystem model or prototype demonstration in a relevant environment (Ground or Space)
- Component and/or breadboard validation in relevant environment
- Component and/or breadboard validation in laboratory environment
- Analytical and experimental critical function and/or characteristic proof-of-concept
- Technology concept and/or application formulated
- Basic principles observed and reported

Nanomaterials: Fundamentals to Applications

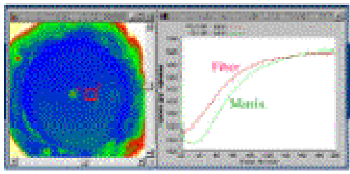
Growth/Production
Laser and HiPco Production and Diagnostics

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

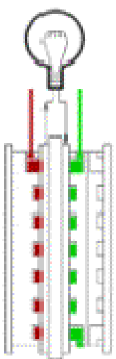
Processing
Purification
Functionalization
Dispersion
Alignment

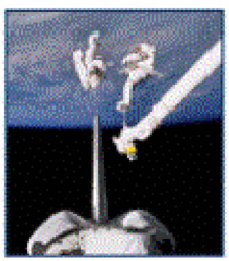
Collaboration
Academia, Industry, Government

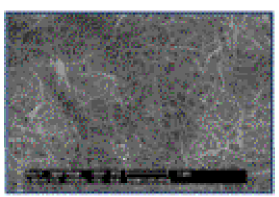
Applications For Human Spaceflight



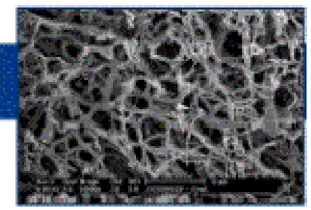
Single Fiber Thermal Diffusivity


Fuel Cells

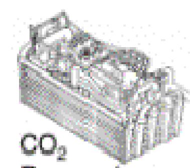

Ultracapacitors (SAFER)

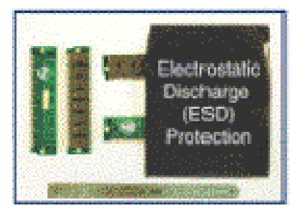

Nanofiltration

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			


Ceramic Nanofibers (TPS)

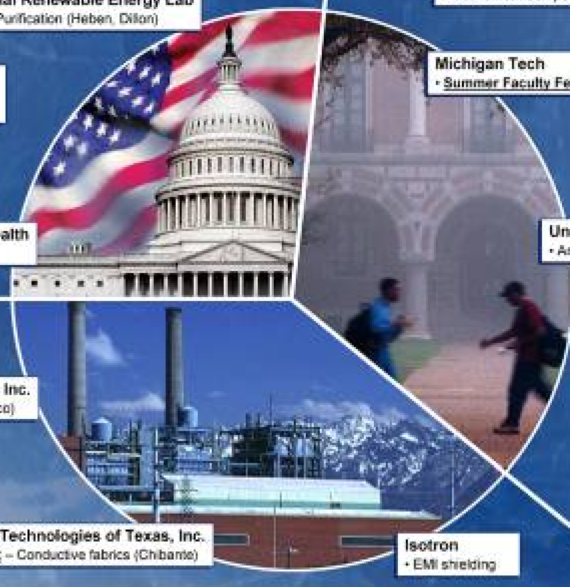

High Thermal Conductivity Fabrics


CO_2 Removal



Electromagnetic Shielding

JSC Nanomaterials Group Collaborations



Government

National Institute of Standards and Technology
- Development of nanoscale measurement standards (Frieman)

NASA Langley Research Center
- Production / purification (JSC) for use in SWNT composites (Siochi, Park, Smith)

Central Intelligence Agency
- Nanotube characterization (Carr)

Oak Ridge National Lab.
- CNT production, purification and characterization (Geohegan)
- Thermal characterization (Wang)

NASA Ames Research Center
- Nanotubes (JSC) for sensors / modeling of HiPco (Meyyappan, Srivastava)

National Renewable Energy Lab
- CNT Purification (Heben, Dillon)

NASA Glenn Research Center
- Functionalization, purification, high temp. mat'ls (Meador, Gray)

Air Force Research Lab.
- Composites, characterization, purification (Maruyama, Strong)

NASA Marshall Space Flight Center
- Nanotubes, MMCs (Gill, Hudson)

Naval Research Lab.
- Composites (Imam, Pehrsson)

Los Alamos National Lab
- Purification (O'Connell)

National Institute for Occupational Safety and Health
- Nanotube toxicology studies (Shvedova)

Academia

NASA-URETI: Texas A&M, Rice, UT Arlington, TSU, PrairieView A&M and UH
- Nanotube characterization
- Radiation protection
- Mechanics / composites

Rice University
- Advanced Nanotechnology Mat'ls and Applications (Smalley, Tour, Barrera)
- Computational Mat'ls Sci. (Yakobson)
- Nanoshells (Halas)

University of Houston
- GSRP, year 3 of 3 – Polymer chemistry, dispersion, composites (Mitchell, Krishnamoorti)

Michigan Tech
- Summer Faculty Fellow - Composites (Caneba)

UC Riverside
- Purification / characterization (Haddon)

Georgia Tech
- Nanotube composite films (Ready)

University of Paris 13
- Arc process (Farhat)

University of Pennsylvania
- CDDF - Thermal Mgmt. Mat'ls (Fischer)
- Composites (Luzzi, Winey)

University of Florida
- Isolated SWNTs (Rinzler)

University of Tennessee, Knoxville
- Nanoindentation (Penumadu)

Northwestern
- Nanomechanics (Ruoff)

University of Oklahoma
- Thermal stability of nanotubes (Resasco)

LeTourneau University
- Summer Faculty Fellow Nanotube growth process (DeBoer)

University of California - Davis
- Nanocrystalline Ceramics (Mukherjee)

Penn State
- Purification / characterization (Eklund)

University of Texas - Tyler
- Summer Faculty Fellow – CFD of Laser process (Greendyke)

Wake Forest
- Characterization of nanotubes (Carroll)

Industry

SouthWest NanoTechnologies, Inc.
- SBIR - Nanotube production (Resasco)

Carbon Nanotechnologies, Inc.
- Production, purification, applications (Smith)

Zyvex
- SBIR – Dispersion (Randall)

NanoTechnologies of Texas, Inc.
- SBIR – Conductive fabrics (Chibante)

Isotron
- EMI shielding

Hamilton-Sundstrand
- CO_2 Scrubber (Papale)

Resolution Performance Products
- Epoxy / nanotube composites (Stark)

Inorganic Specialists
- SBIR - Electrochemical capacitors (Firsich)

Nantero, Inc.
- NanoRAM development (Siegel)

ReyTech
- SBIR – Ultracapacitors (Reynolds)

Ionwerks
- Mass spectrometry (Schultz)

COI Ceramics
- RTF – Ceramic / nanotube composites (Riedell)

Nanospectra
- Thermal control coatings (Watkins)

Eikos
- EMI Shielding (Glatkowski)

Materials and Electrochemical Research
- SBIR - Nanotube production (Loutfy)

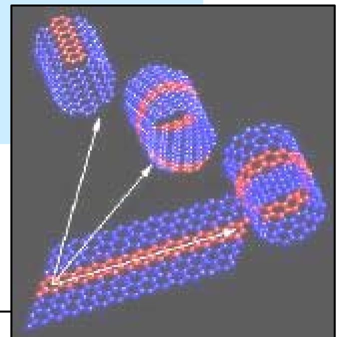
Honda
- Magnetic characterization (Harutyunyan)

GB Tech
- Fuel cells / CO_2 scrubber (Huffman)

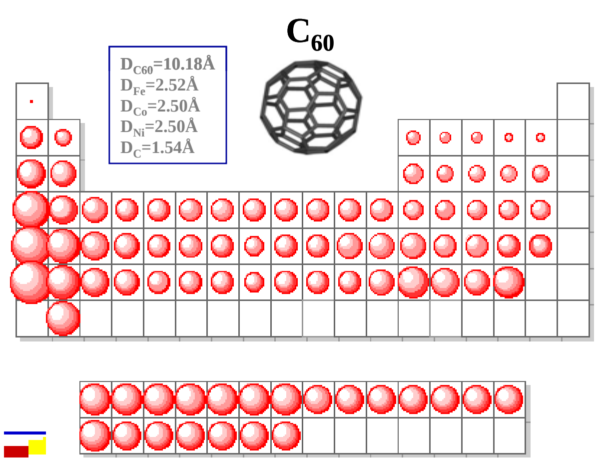
Nanomaterials: Single Wall Carbon Nanotubes

Unique Properties

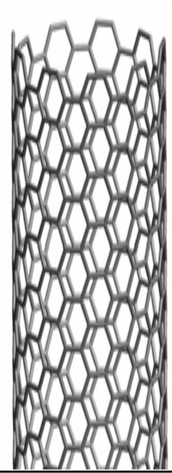
- Exceptional strength
- Interesting electrical properties (metallic, semi-conducting, semi-metal)
- High thermal conductivity
- Large aspect ratios
- Large surface areas



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



Single Wall Carbon Nanotube



Possible Applications

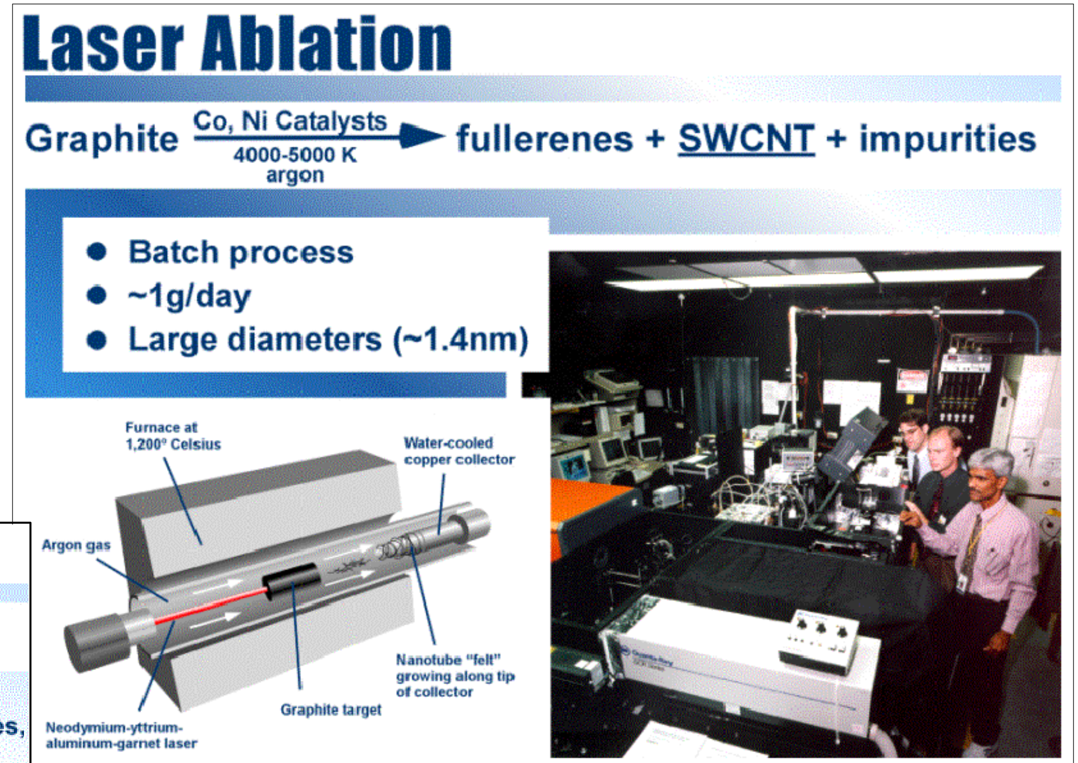
- High-strength, light-weight fibers and composites
- Nano-electronics, sensors, and field emission displays
- Radiation shielding and monitoring
- Fuel cells, energy storage, capacitors
- Biotechnology
- Advanced life support materials
- Electromagnetic shielding and electrostatic discharge materials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

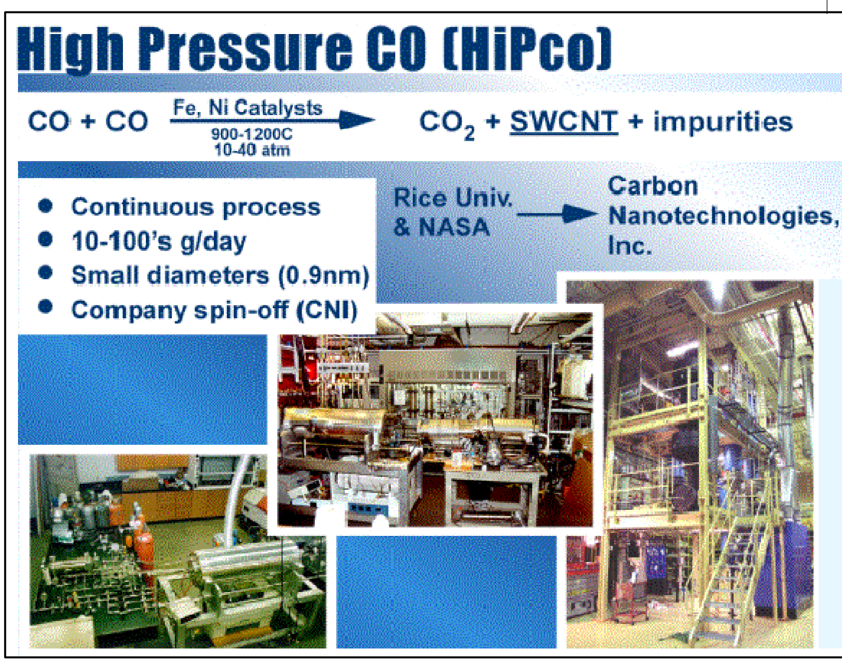
Current Limitations

- 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

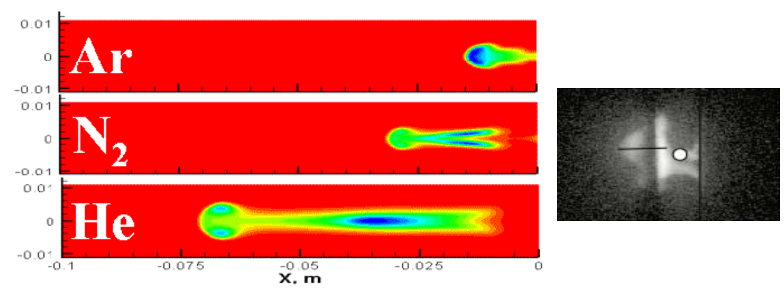
Growth, Modeling, Diagnostics and Production

Objective: Ensure a reliable source of single wall carbon nanotubes with tailored properties (length, diameter, purity, chirality)

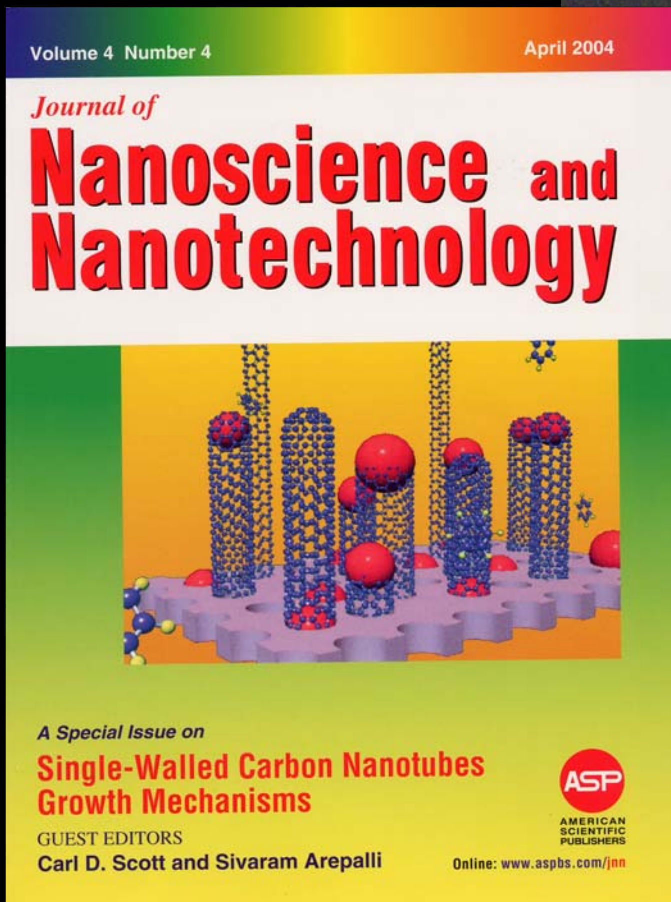


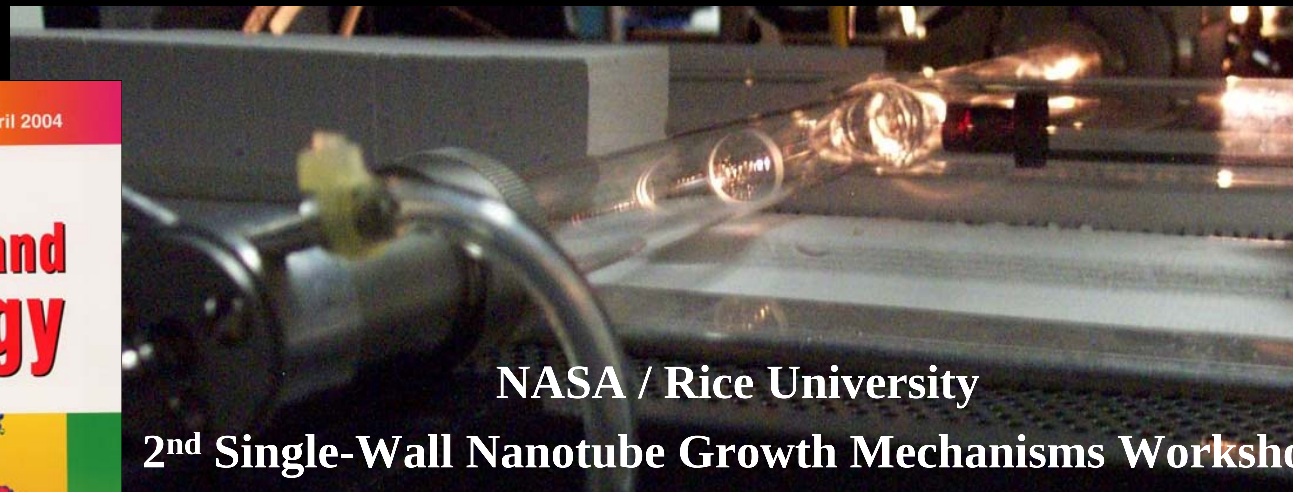


Modeling, Diagnostics, and Parametric Studies



Growth, Modeling, Diagnostics and Production



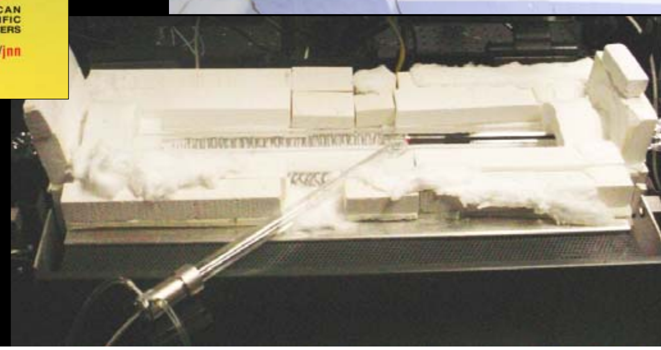


NASA / Rice University

2nd Single-Wall Nanotube Growth Mechanisms Workshop

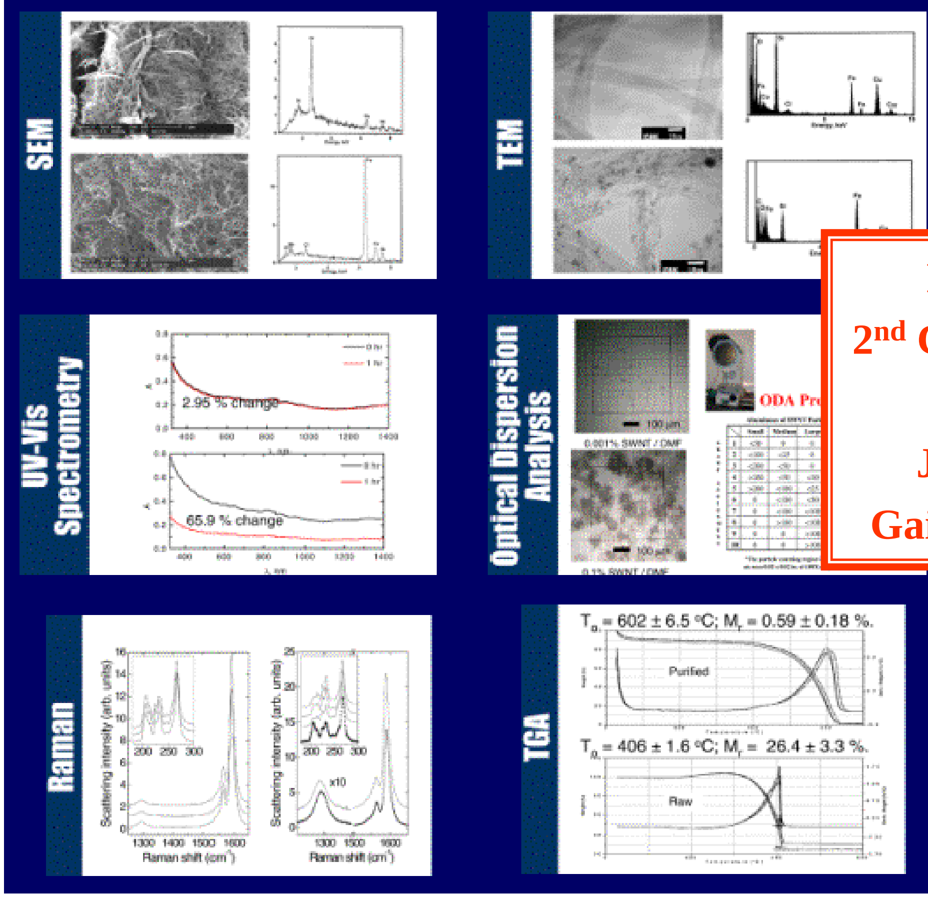
April 2005

Guadalupe River Ranch, Texas



Characterization: Purity, Dispersion & Consistency

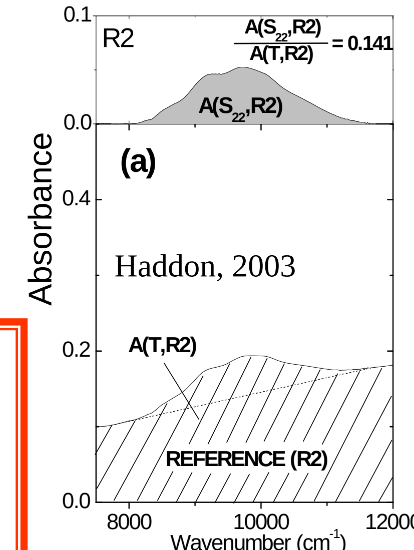
Standard Nanotube Characterization Protocol

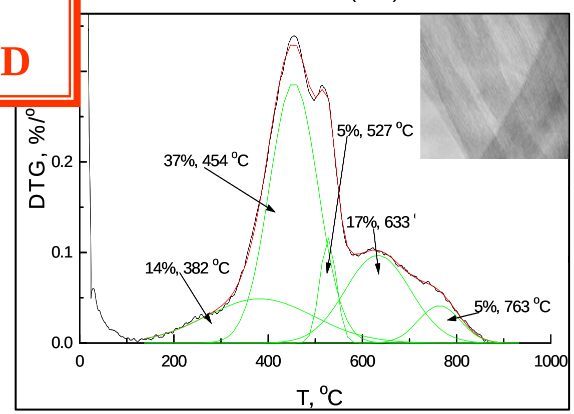


Arepalli, et al., Carbon, 2004

NASA/NIST
2nd Characterization Workshop
January 2005
Gaithersburg, MD

New Purity Reference Standard





Applications for Human Space Exploration

Power / Energy Storage Materials
- Proton Exchange Membrane (PEM) Fuel Cells
- Supercapacitors / batteries

Advanced Life Support
- Regenerable CO_2 Removal
- Water recovery

Multi-functional / Structural Materials
- Primary structure (airframe)
- Inflatables

Thermal Management and Protection
- Ceramic nanofibers for advanced reentry materials
- Passive / active thermal management (spacesuit fabric, avionics)

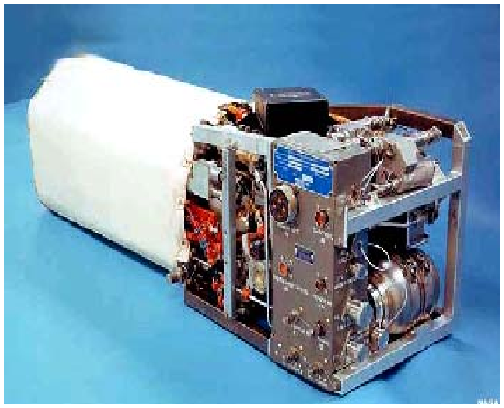
Electromagnetic / Radiation Shielding and Monitoring
- ESD/EMI coatings
- Radiation monitoring

Nano-Biotechnology
- Health monitoring (assays)
- Countermeasures

Electrical Power / Energy Storage Systems

Advanced Power Generation: Hybrid Systems

Fuel Cell



- Continuous energy supply
- High energy density
- Low power density

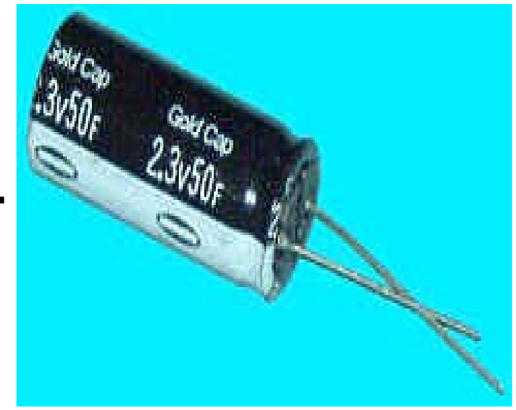
+

Battery

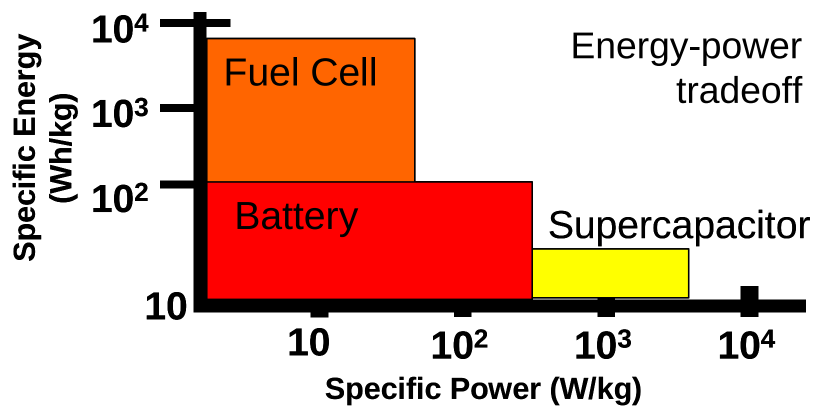
- Smaller, lighter, longer life with hybrid
- Intermediate power density
- Intermediate energy density

+

Supercapacitor

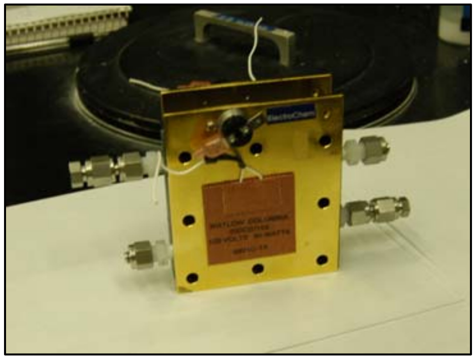


- Pulse power source
- Fast charge/discharge
- Very high power density
- Virtually unlimited cycle life

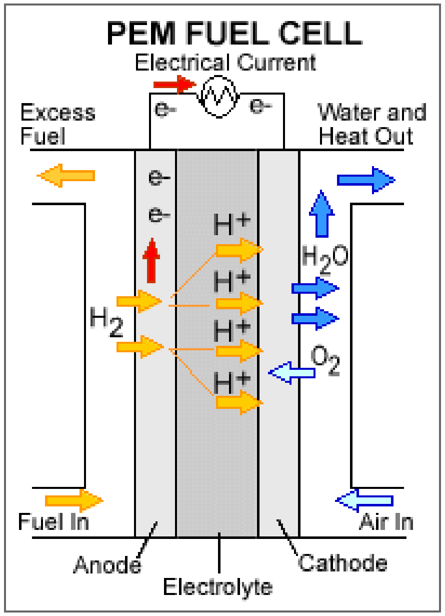


Advanced PEM Fuel Cells – Nanotube Electrodes

- Carbon nanotube electrode assemblies for proton exchange membrane (PEM) fuel cells
- Membrane Electrode Assembly (MEA) formed from a Nafion™ membrane sandwiched between nanotube electrodes with Pt catalyst



- **Increased surface area of the electrodes**
- **Enhanced thermal management**
- **Reduce Ohmic losses – increase efficiency**
- **Higher power density**
- **Small diameter HiPco tubes may enhance H_2 dissociation – optimized porosity**
- **More uniform current density**



Source: www.eere.energy.gov

Advanced PEM Fuel Cells - Characterization

Characteristic	Technique/ Instrument	Destructive	When	Results
Amount of Pt, Fe, Co, Ni	X Ray Photoelectron/ Fluorescence Spectroscopy	no	After BP is baked (Part 5);	Quan
Platinum Dispersion	Scanning Electron Microscopy (SEM)	yes	After BP is baked (Part 5)	Qual
Platinum Dispersion	Transmission Electron Microscopy (TEM)	yes	After BP is baked (Part 5)	Qual
Electrical Conductivity	Probe Meter	no	After MEA is made (Part 7)	Qual
Surface Area & Porosity	Brunauer, Emmett, and Teller Analysis (BET)	yes	After BP is (1) made and (2) baked (Part 4 and Part 5)	Quan

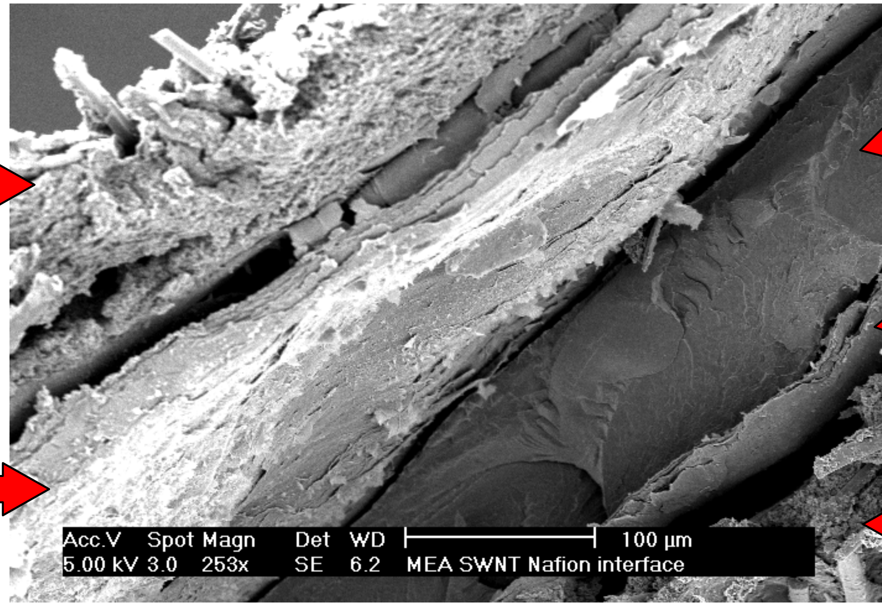
Characteristic	Technique/ Instrument	Destructive	When	Results
Mass	Scale	no	After BP is (1) made and (2) baked (Part 3 and Part 5)	Quan
Thickness	Randall&Stickney Dial Gauge	no	After BP is (1) made and (2) baked (Part 3 and Part 5)	Quan
Interface and Thickness	Freeze Fracture then SEM	yes	After MEA is made (Part 7)	Qual/Quan
Interface	Flash IR Thermography	no	After MEA is made (Part 7)	Qual
Interface	Current Voltage Curve	no	During Fuel Cell Testing	Quan

Advanced PEM Fuel Cells - Characterization

Prototype Membrane Electrode Assembly

Carbon Fiber Gas Diffusion Layer (GDL)

Single Wall Carbon Nanotube (SWCNT) Electrode

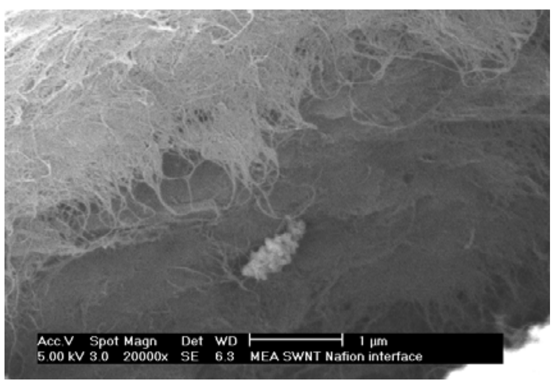


Nafion™ Membrane

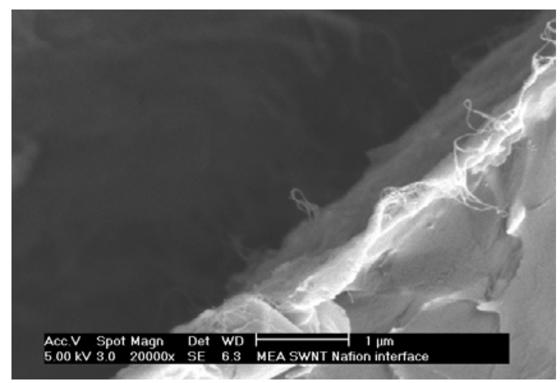
SWCNT Electrode

Carbon Fiber (GDL)

SWCNT interface in MEA



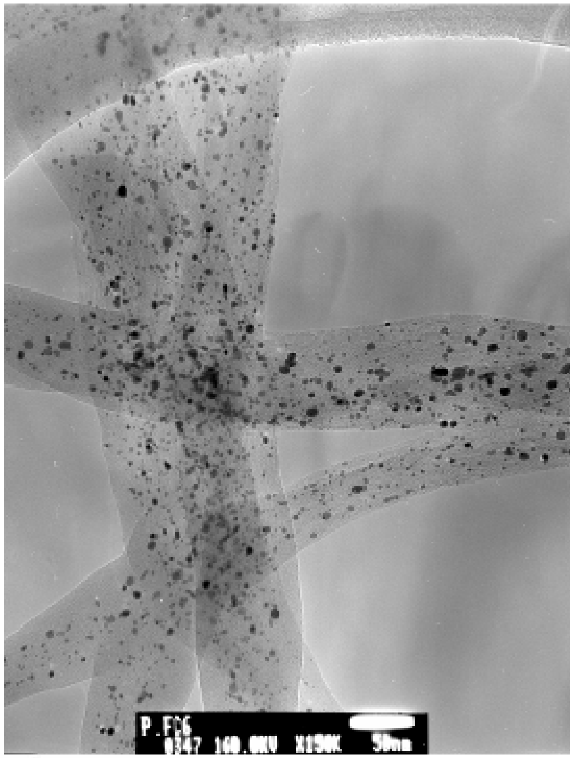
Nafion™ interface in MEA

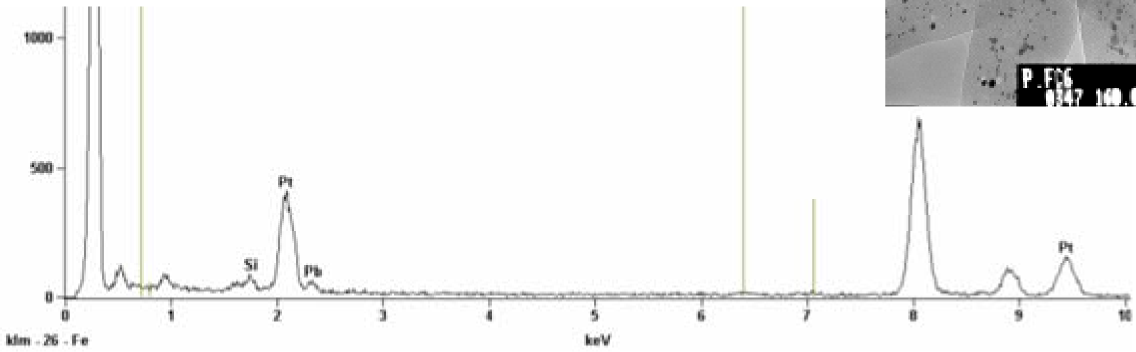


Characterization PEMFC: TEM of Electrodes Made with Purified SWCNTs

TEM provides particle size distribution and EDX Shows elemental composition.

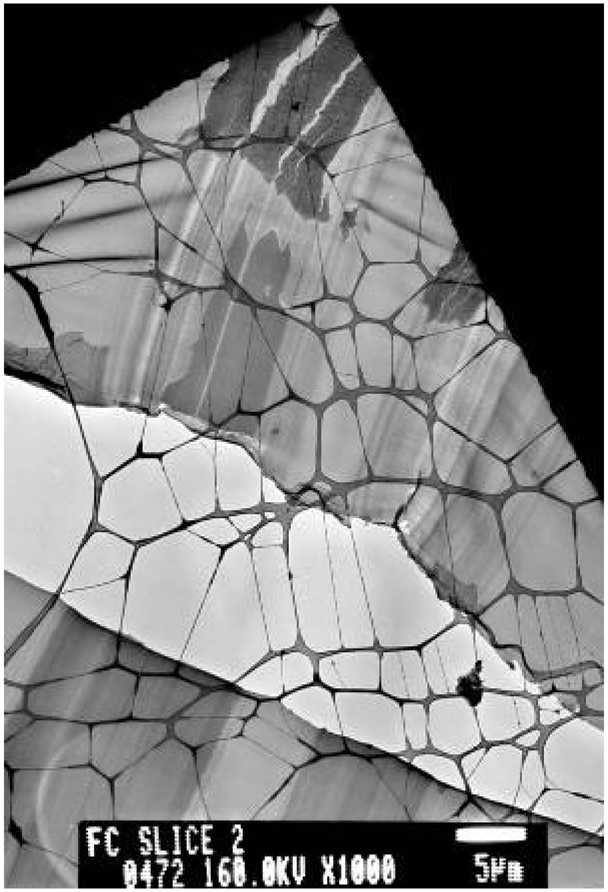
- EDX data does not indicate the presence of Fe (would show up at about 6.4 keV).
- EDX does indicate the presence of Pt, therefore we presume that the visible nanoparticles are composed of Pt.
- TEM shows a range of Pt particle sizes between 2nm and 10nm.
- XPS data indicates that Pt is metallic. This indicates complete decomposition of the precursor.

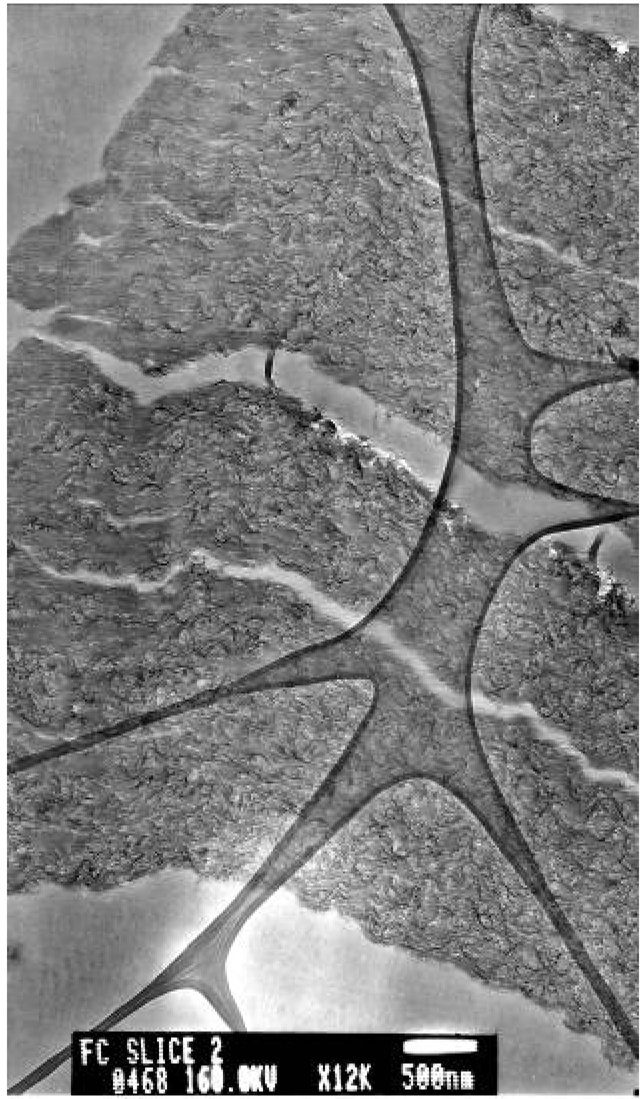


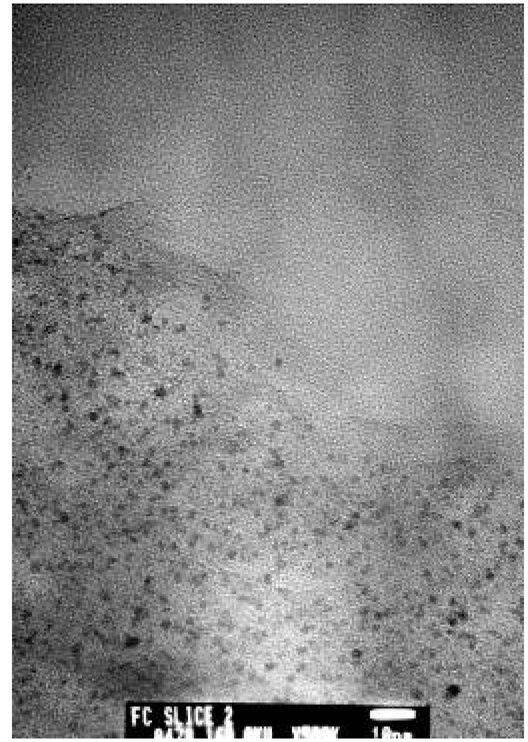


Characterization PEMFC: TEM of Electrodes Ultramicrotomy

TEM Ultramicrotomy Study to characterization interface between GDL, electrodes and Nafion



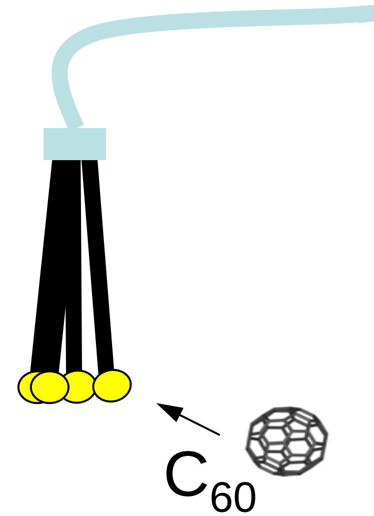




PEMFC

- Developed Characterization protocol
- Test capability at NASA JSC
- Achieving catalyst size and performance
- Higher performance at lower current loading – increased PEMFC kinetics

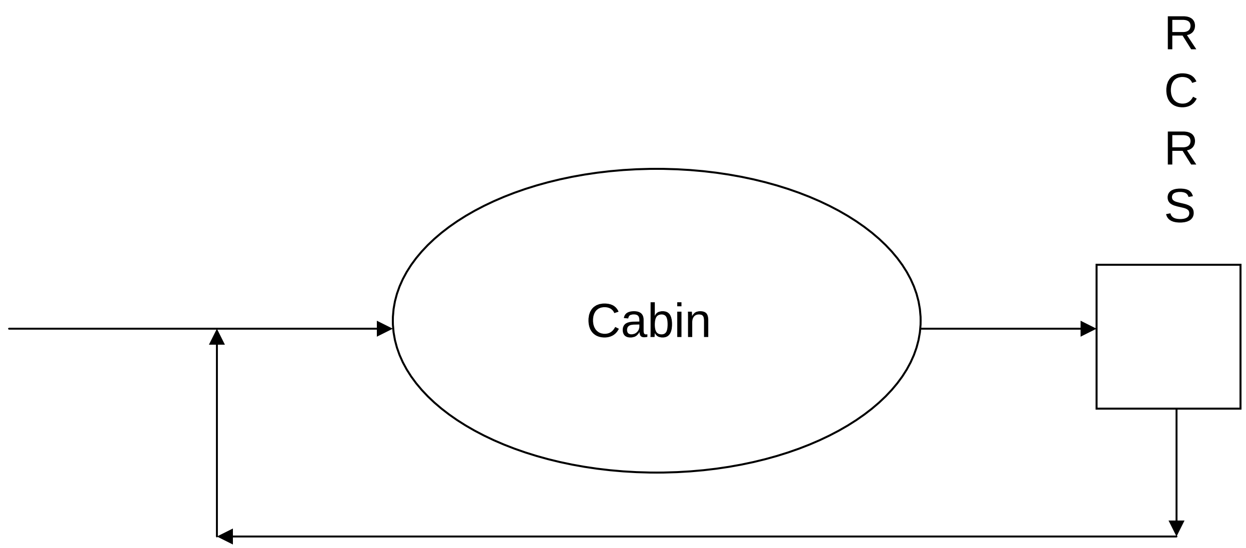
Water Purification



- 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 Due December 2005

Air Revitalization: CO_2 Removal

- Remove CO_2 from cabin air in order to extend the use of cabin air supplies
- Only a small amount of CO_2 can contaminate a large amount of cabin air



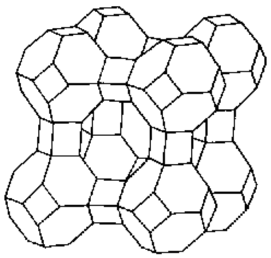
Air Revitalization: Some Current Technologies

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

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

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

Zeolite 5A: Physisorption of CO_2



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

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

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

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

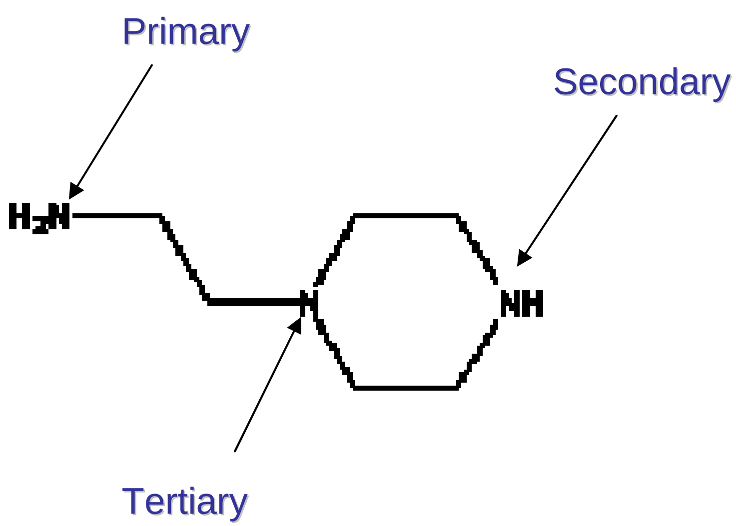
$$Ag_2CO_3 \xrightarrow[220C]{\Delta} Ag_2O + CO_2$$

Supported Amines for Air Revitalization

$$R_1R_2NH + CO_2(aq) \xleftrightarrow{K_1} R_1R_2NH^+CO_2^- \qquad (1)$$

$$R_1R_2NH + R_1R_2NH^+CO_2^- \xleftrightarrow{K_{c2}} R_1R_2NH^+ + R_1R_2NCO_2^- \qquad (2)$$

$$R_1R_2R_3N + H_2O + CO_2(aq) \xleftrightarrow{K_3} R_1R_2R_3NH^+ + HCO_3^- \qquad (3)$$



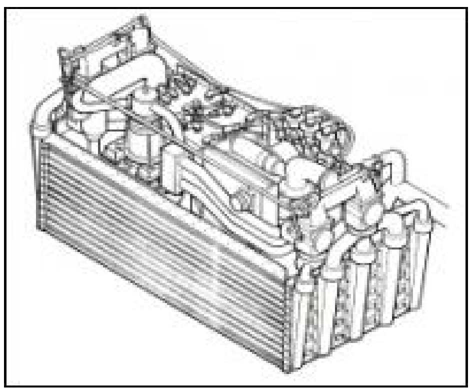
N-aminoethylpiperazine

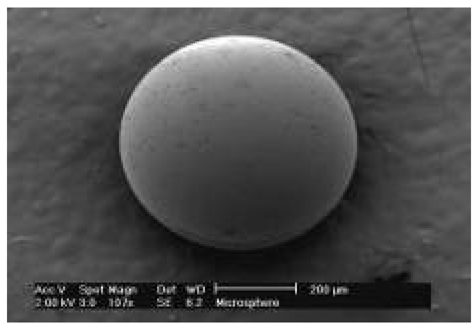
- Catalyzed by moisture
- Depending on their bonding amines have varying degrees of affinity for CO_2 capture and desorption
- Primary binds CO_2 tightly, thus inhibiting desorption while tertiary amines bind CO_2 poorly
- Secondary amines are preferred for pressure swing

The State of the Art in Amine Systems

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





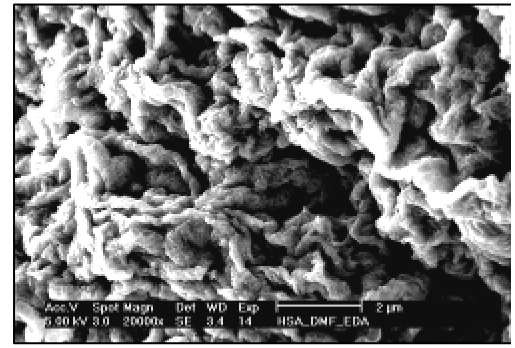
Polymer Bead **and** Aluminum Structure

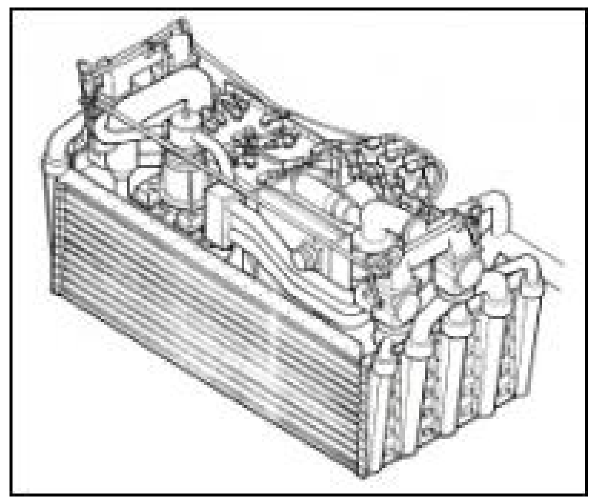
Carbon nanotubes may offer a thermally conductive high surface area light weight support material for this application

Initial Results and Technology Assessment

Results

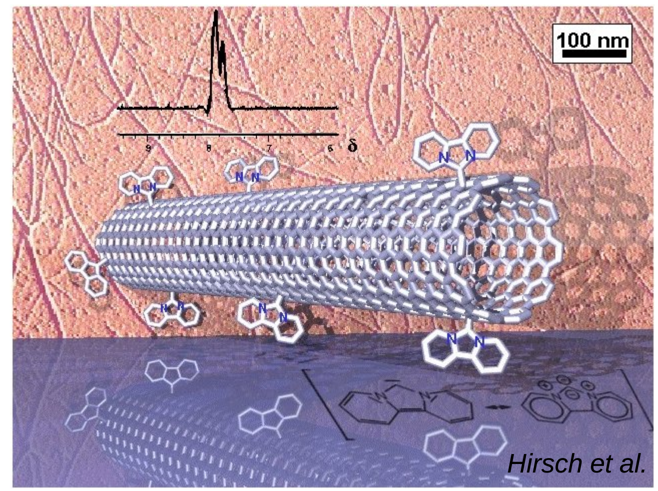
- Carbon Nanotubes have high surface area: bucky pearls, fibers, bucky paper
- TGA experiment: the amine is reactive with the CO_2 gas stream
- Poor adherence to nanotube surface - requires a specific pore size and shape
- We need a better way to integrate the support phase with the amine



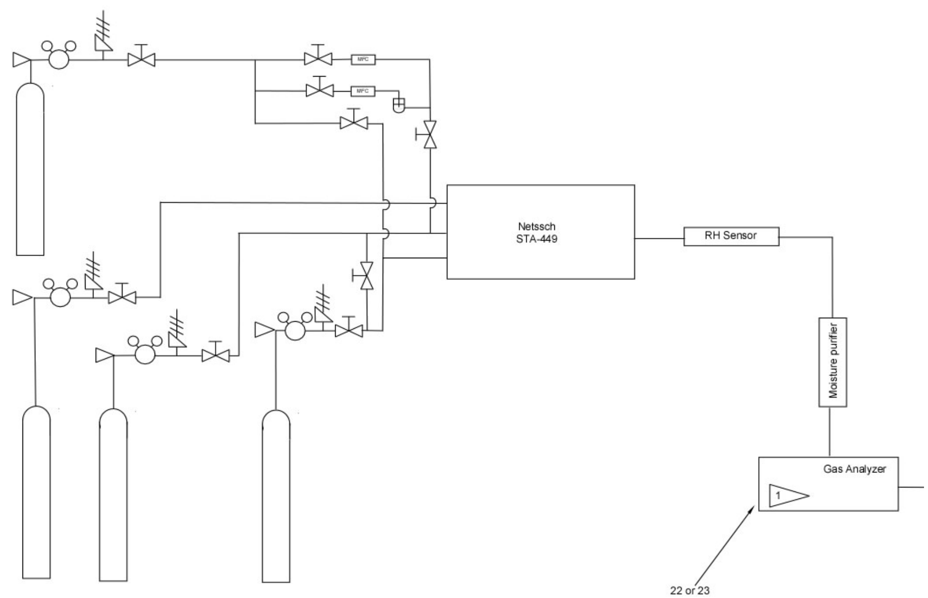


Materials Development and Testing

- Collaborations for functionalization of SWCNTs
- Dr. W. E. Billups group (Rice University)
- Dr. J. Tour group (Rice University)

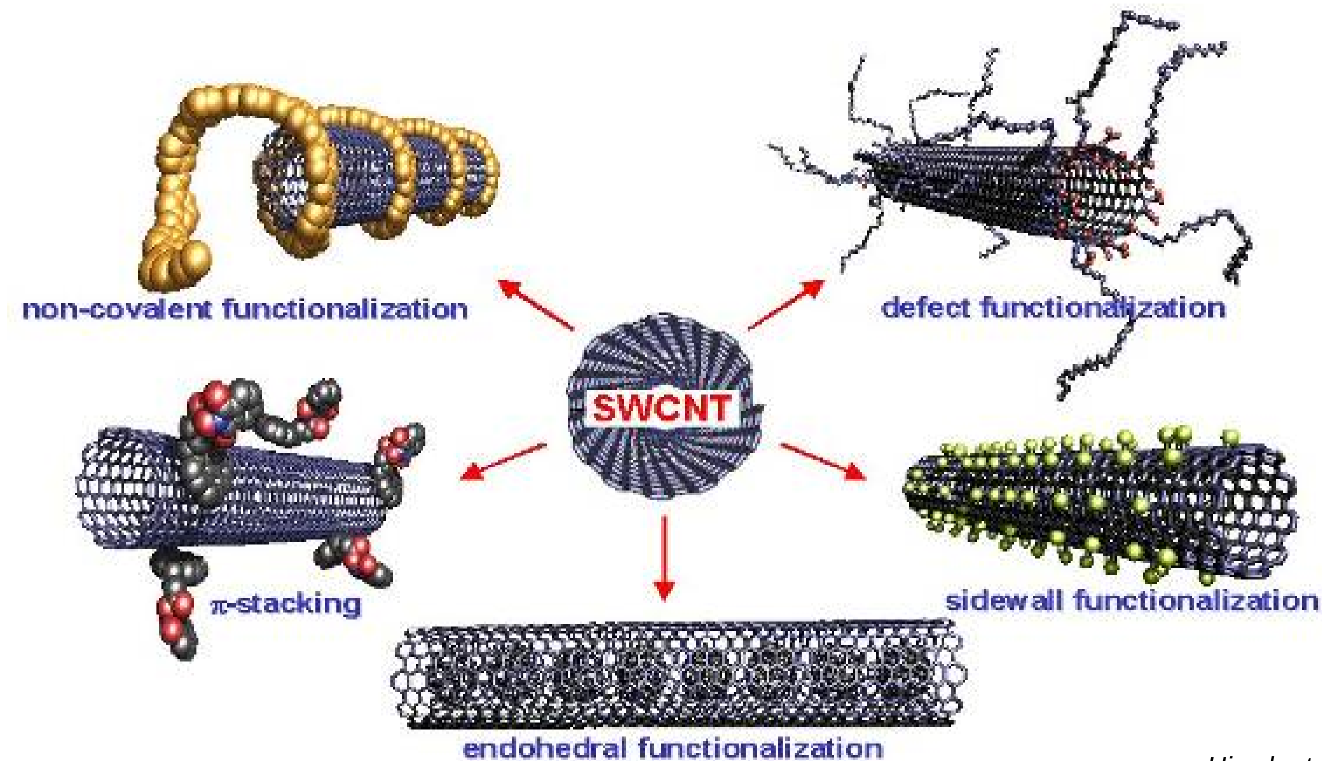


- Collaboration with Dr. T. Filburn (University of Hartford)
  - Determine the types of amines that would be suitable for spaceflight needs
  - Testing methods for equilibrium adsorption and desorption and well as cyclic behavior



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



Hirsch et al.

The argument for functionalization

- Amenable to repeated cycling
  - Materials are thermally stable up to 100 C. (Thermal desorption takes place at 50 – 60 C)
  - 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

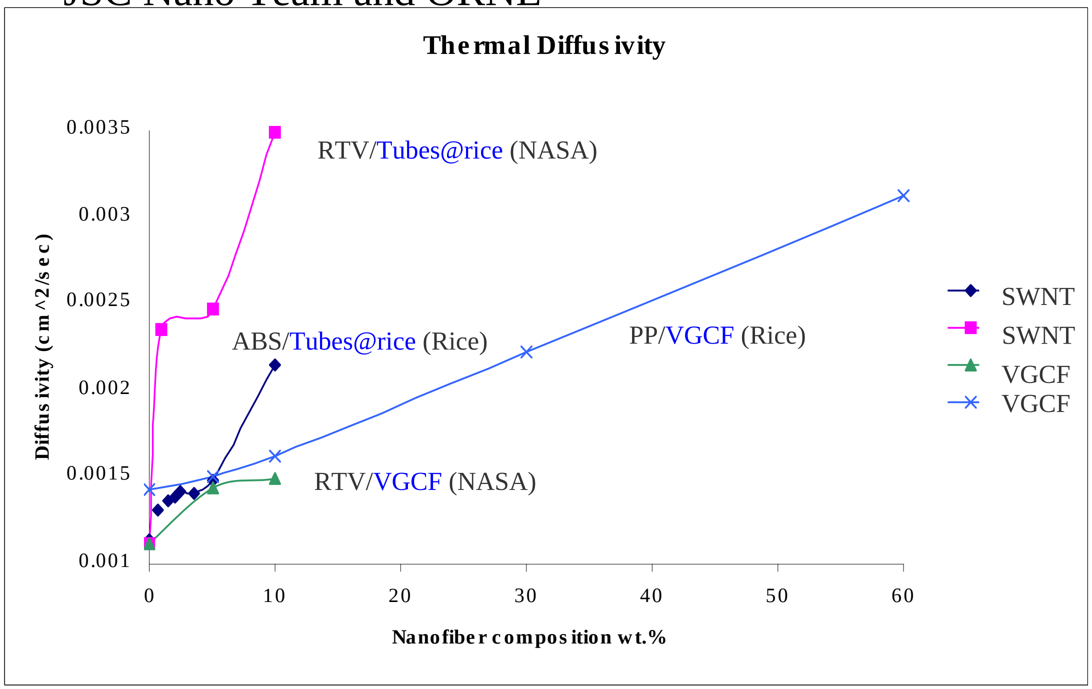
Active / Passive Thermal Management Materials

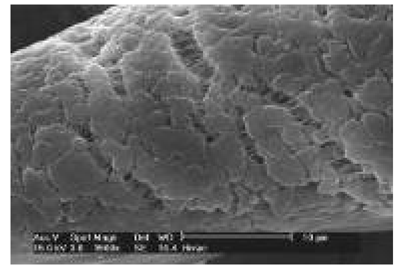
• SWNT thermal properties are extremely anisotropic; SWNT axial conductivity is comparable to that of diamond (2150 W/m-K)

• Nylon Spandex/SWNT fabric improves crew member's thermal comfort and increases heat transfer rate to EMU sublimator (SBIR)

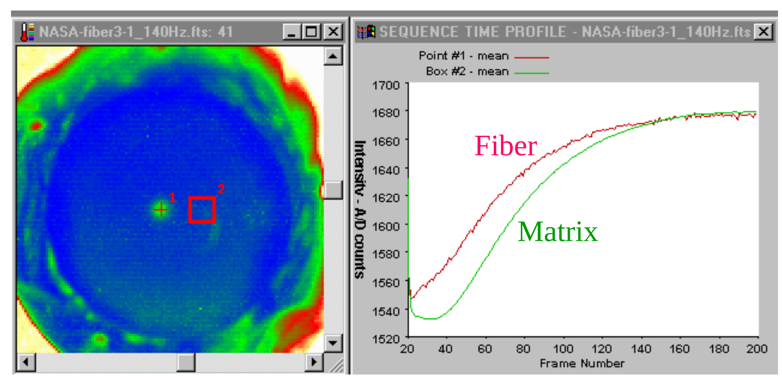
• Active heat acquisition and transport applications in concept stage (advanced coldplate, interface, fluids)

• New single-fiber thermal diffusivity tool developed by JSC Nano Team and ORNL





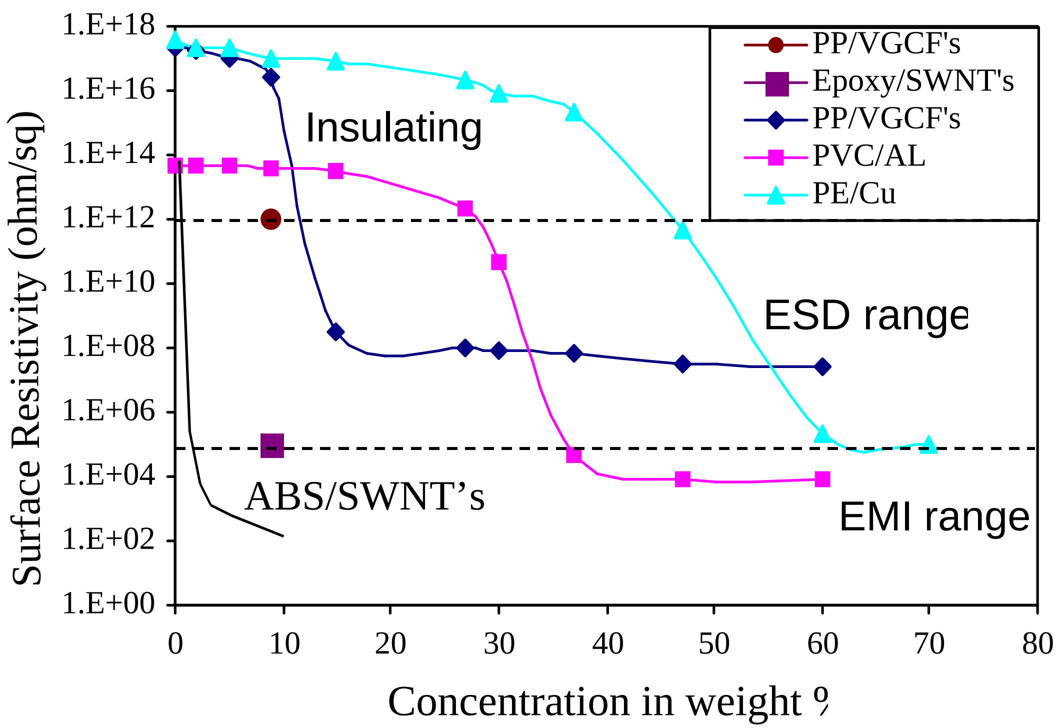
Nylon Spandex/SWNT Fabric for Spacesuits



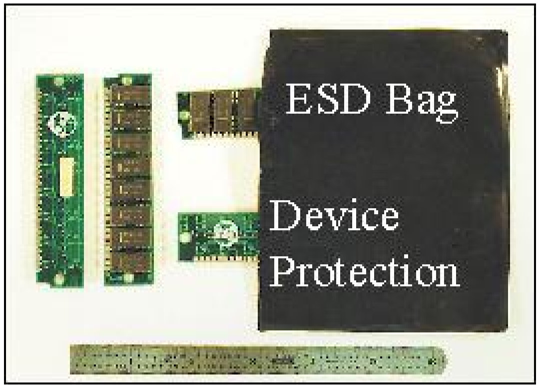
Single Fiber Thermal Diffusivity (JSC and ORNL)

ESD and EMI Materials with Nanotubes

- Application
  - SWNTs in a polymer at low concentrations to shield electronics from electromagnetic interference (EMI) and for electrostatic discharge (ESD) protection of sensitive electronics components.
  - Advantages – lightweight, humidity independent, flexible, ideal for coatings



E.V. Barrera et al., Rice University



- **Testing plan in work with EV (EMI)**
- **Industry-produced composites tested in RITF (ESD)**

Carbon Nanotube Radiation Dosimeter

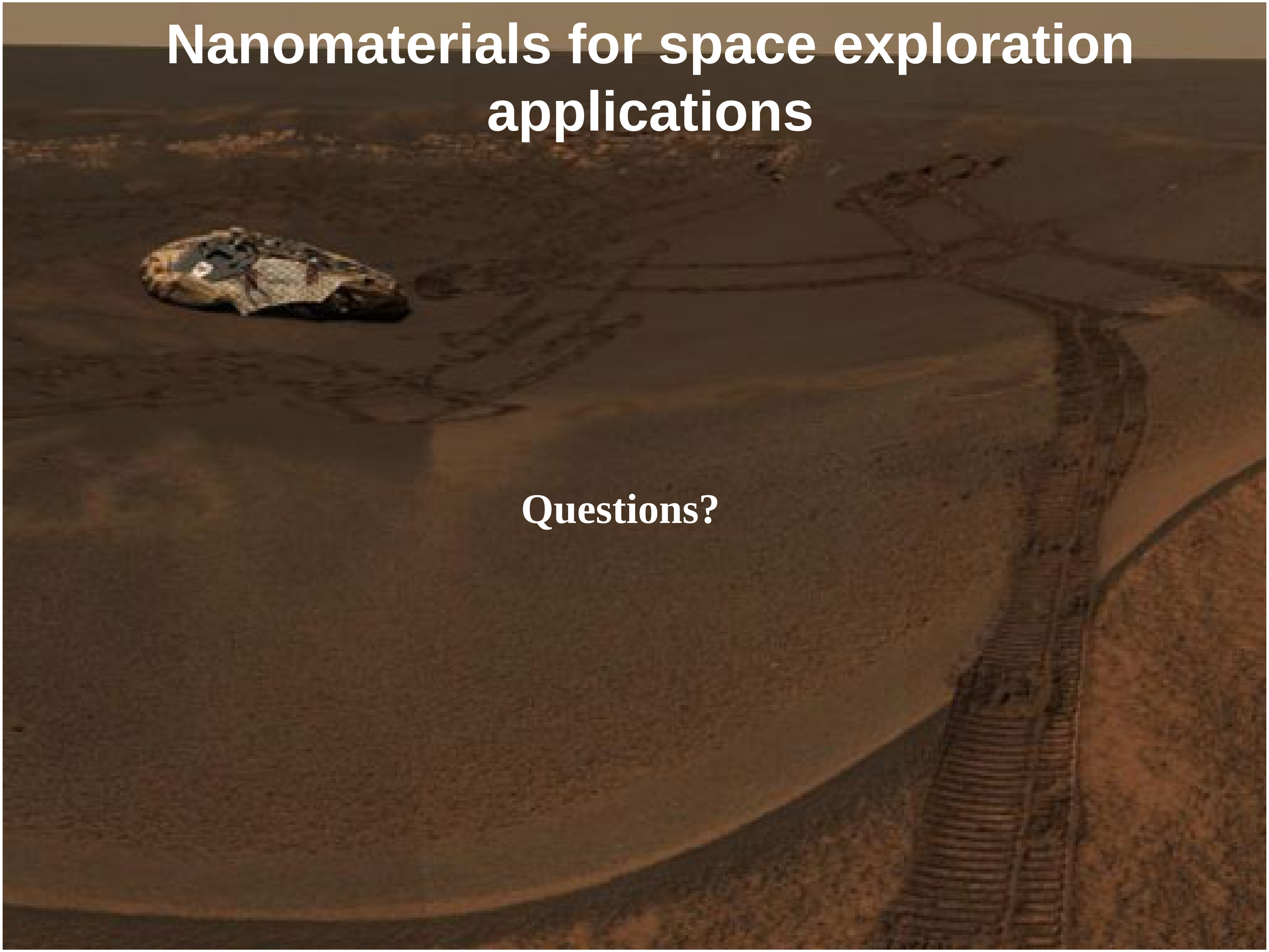
Compelling need to directly measure the radiation environment of spacecraft and compare to models for safety to humans for EVA and future space travel

- SWNTs respond at the particle level—radiation particle bombardment may be quantitatively detectable
- Fly initially as a passive experiment to gather real-time radiation dose on orbit
- Applicable for commercial usage by Medical, Nuclear industries

Summary

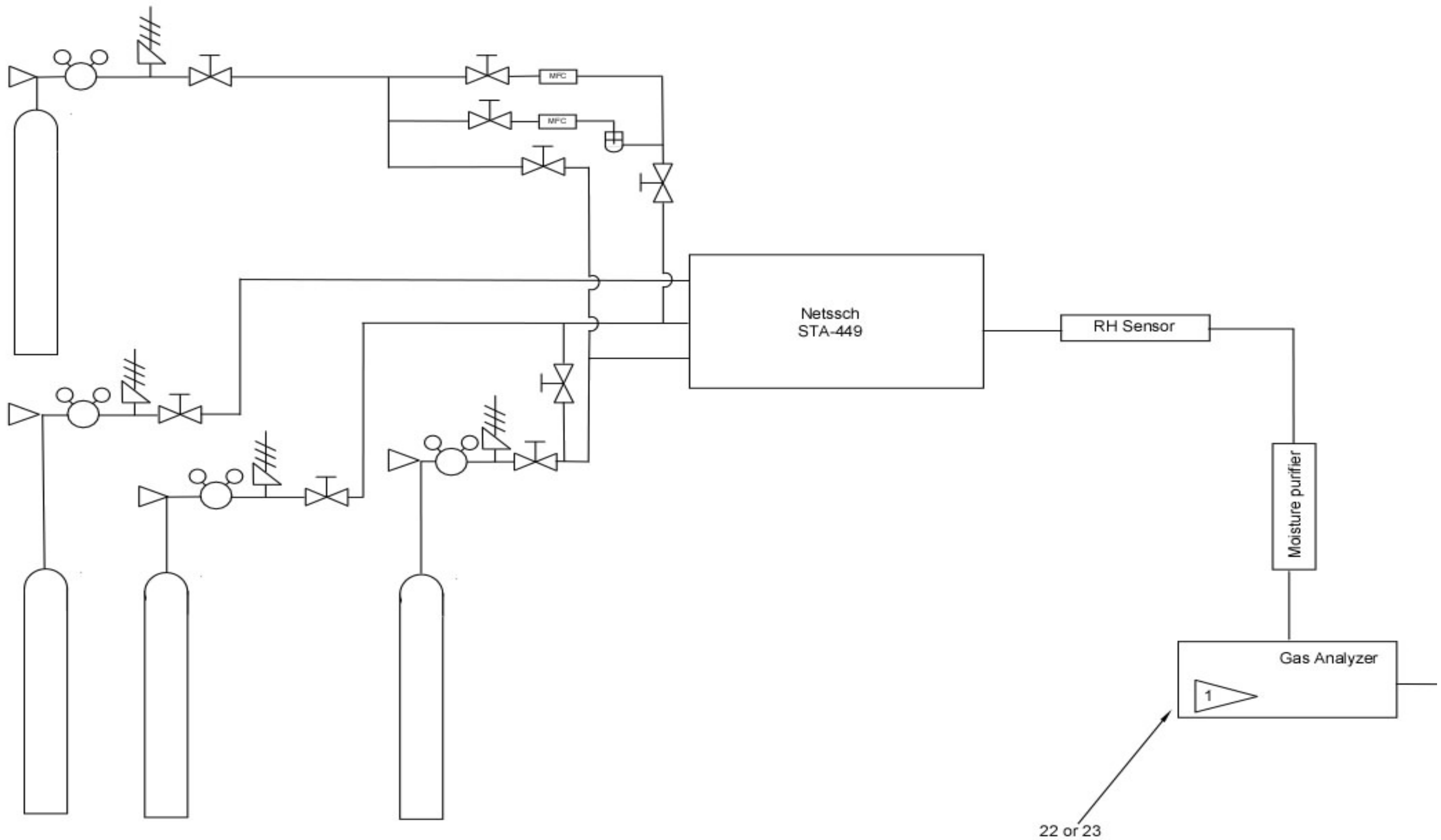
- Overview of NASA JSC NanoMaterials Project
  - Need
  - NanoMaterials Growth
  - NanoMaterials Characterization
  - NanoMaterials Processing
  - NanoMaterials Application
- NanoMaterials for PEMFC
- Presented work for developing solid-supported amine adsorbents based on carbon nanotube materials
  - Materials testing
  - Functionalization of SWCNTs
- Briefly: Other Application areas

Nanomaterials for space exploration applications



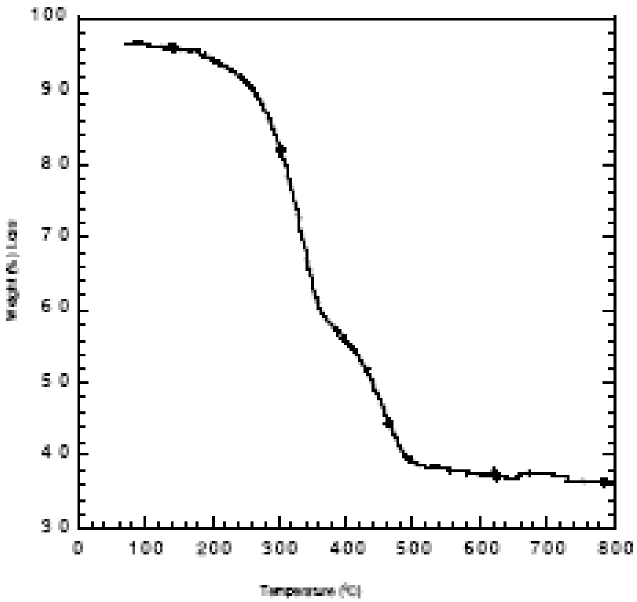
Questions?

Microscale Testing of Equilibrium CO_2 Capture

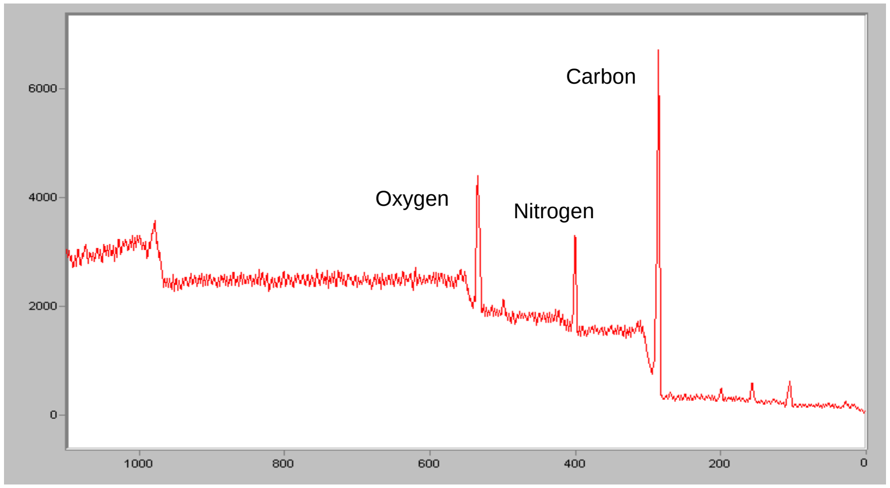


- TGA/DSC experiment: Measure the weight change of a sample upon exposure to CO_2 +H_2O stream – DSC shows heat flow indicative of amine/ CO_2 reaction
- Recent upgrade: Residual gas analyzer measures the change in CO_2 concentration

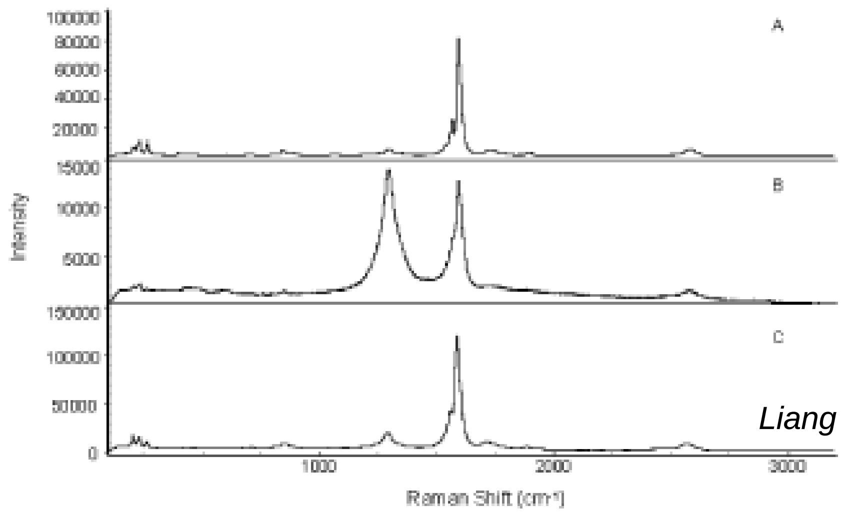
Characterization of Functionalized SWCNTs



TGA for PEI functionalized SWCNTS



XPS Spectrum of L-PEI functionalized SWCNTS



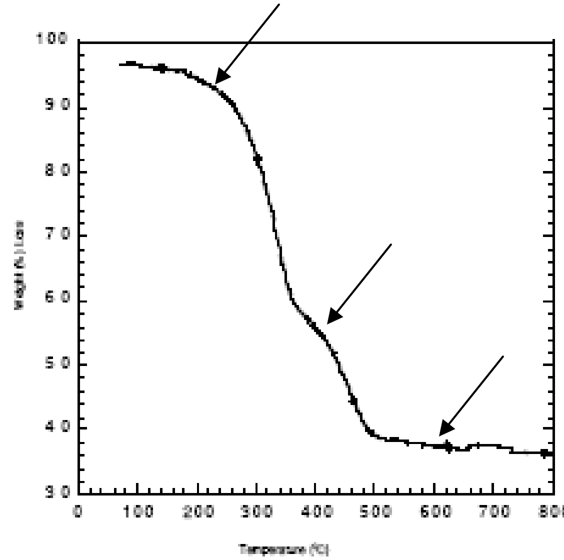
Liang et al. 2004

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

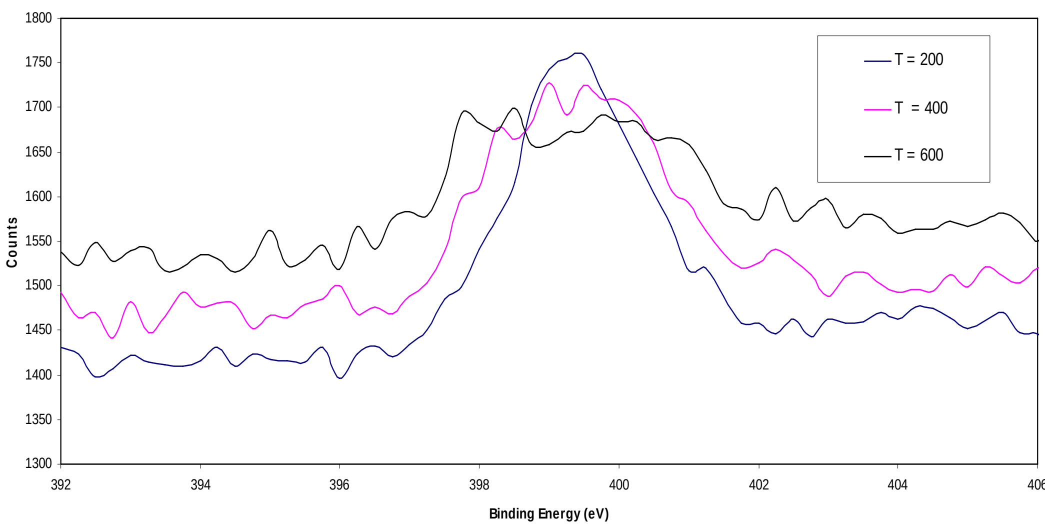
TGA/XPS Study of the Thermal Stability of Functionalized SWCNTs

<u>TGA/XPS study of removal of functional groups</u>

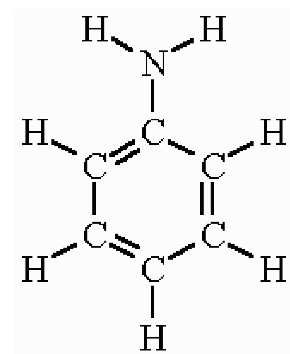
- Heat samples to various temperature and observe weight loss
- Examine XPS peaks characteristic of groups of interest
- Correlate weight loss to loss of functional group



TGA Weight Loss



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



Aniline

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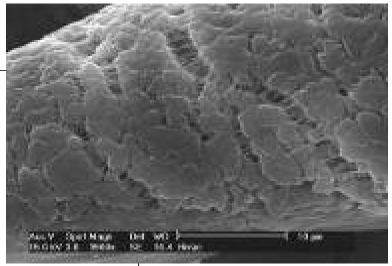
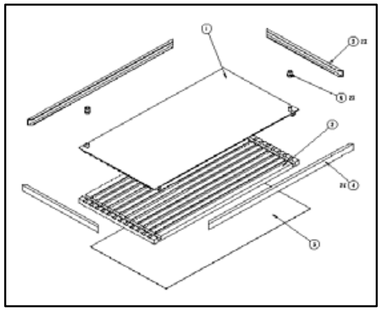
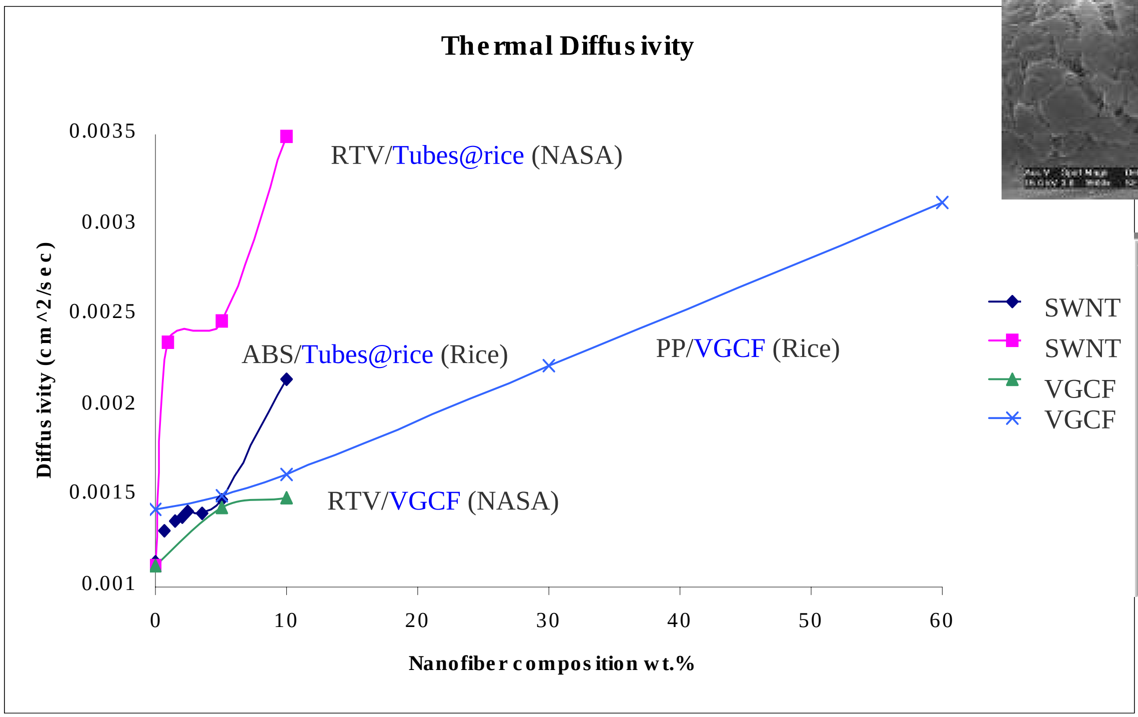
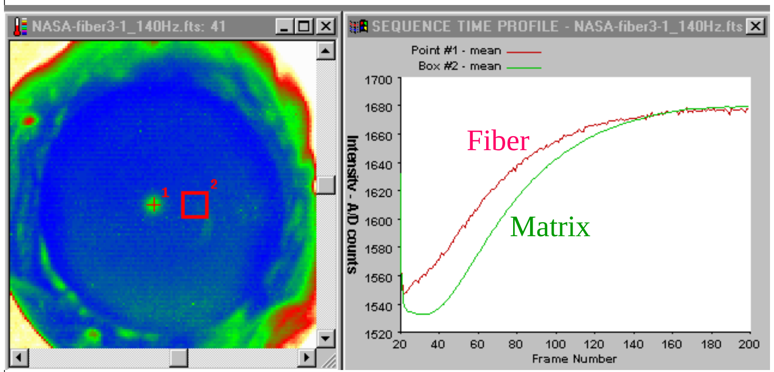




Heat Acquisition
Heat Transport





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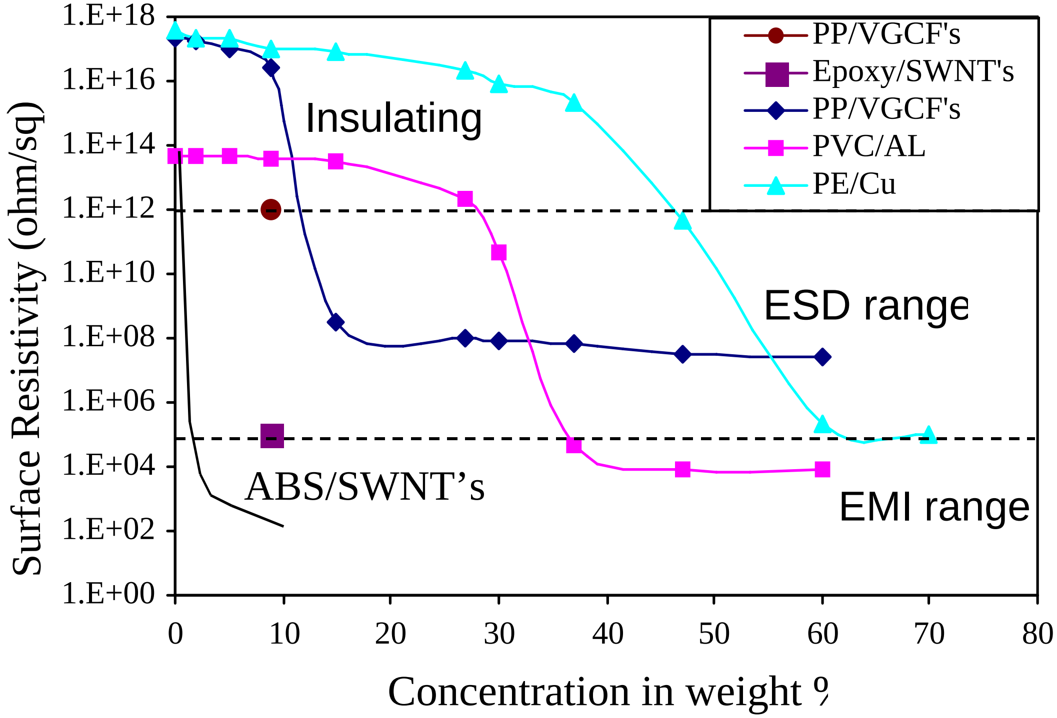
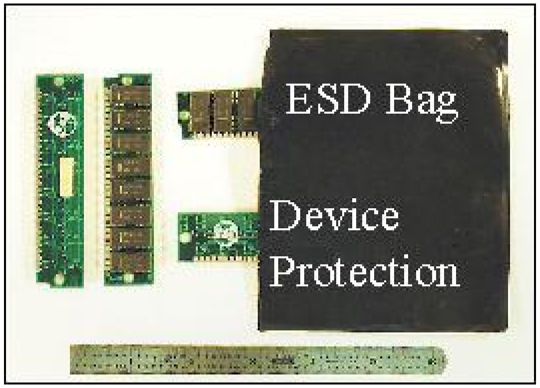


E.V. Barrera et al., Rice University



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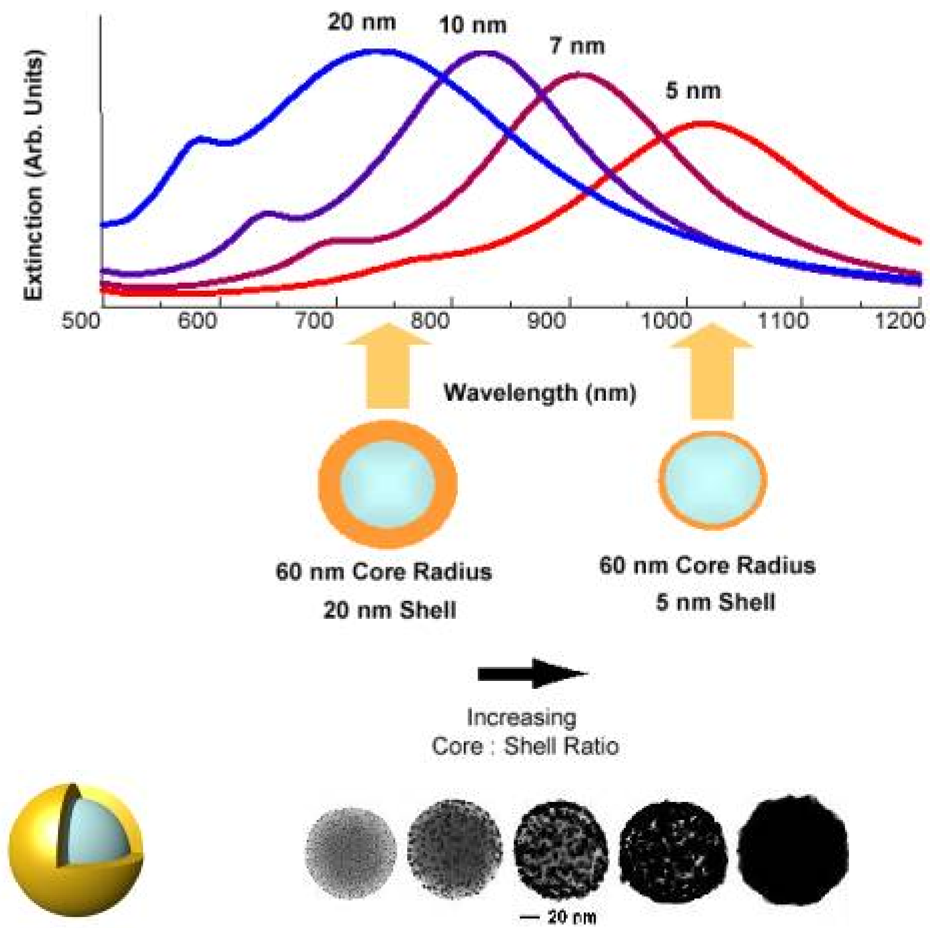
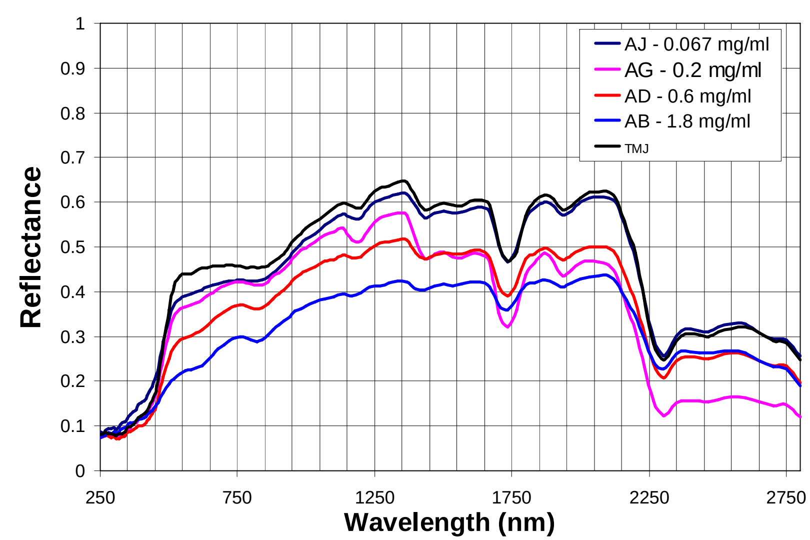
Nanoshells for Thermal Control Coatings



Courtesy of NanoSpectra

- Nanoshells offer possibility of *designing* thermal control coatings
- Thermo-optical properties manipulated by nanoshell geometry
  - ratio of silica core to shell thickness
  - independent of overall organization of nanoshells
- Interested in nanoshell design with low solar absorbtivity and high emittance

TMJ Paint with Varying Nanoshell Concentrations



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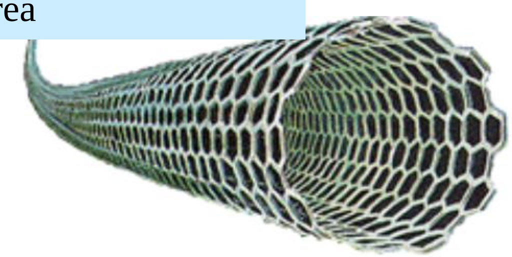
Nanotechnology & Human Spaceflight

Key Enabler to Human & Robotic Exploration

Nano-Engineered Materials
- Truly multi-functional materials
- Best known mechanical, thermal, and electrical properties exist now at the nanoscale
- Highest possible surface area



Human Spaceflight applications will drive unique advances in…
- Safety and Toxicology
- Reliability and Durability

Technology Needs for Long-Duration Human Spaceflight
- Reduced mass / volume
- Greater reliability of materials/systems
- System health monitoring & repair
- Air revitalization
- Water recovery
- Human health diagnosis & treatment
- Radiation protection & detection
- In-space manufacturing

Current Nanoscale R&D on Human Spaceflight Applications
- Electromagnetic Shielding Materials
- Proton Exchange Membrane – PEM - Fuel Cells
- Nanotube-Based Structural Composites
- RCRS - Regenerable CO_2 Removal System
- Ceramic Nanofibers for Thermal Protection Materials
- High Thermal Conductivity Fabric for Spacesuits
- Radiation Resistance/Protection
- Passive Radiation Dosimeter
- Active Thermal Control Systems for Space
- Nanoshells for Thermal Control Coatings