Carbon Nanotube Activities at NASA-Johnson Space Center

Sivaram Arepalli
NASA-Johnson Space Center
Houston, TX 77058

Abstract

Research activities on carbon nanotubes at NASA-Johnson Space Center include production, purification, characterization and their applications for human space flight. In-situ diagnostics during nanotube production by laser oven process include collection of spatial and temporal data of passive emission and laser induced fluorescence from C2, C3 and Nickel atoms in the plume [1]. Details of the results from the “parametric study” of the pulsed laser ablation process indicate the effect of production parameters including temperature, buffer gas, flow rate, pressure, and laser fluence [2]. Improvement of the purity by a variety of steps in the purification process is monitored by characterization techniques including SEM, TEM, Raman, UV-VIS-NIR and TGA. A recently established NASA-JSC protocol [3] for SWCNT characterization is undergoing revision with feedback from nanotube community. Efforts at JSC over the past five years in composites have centered on structural polymer/nanotube systems. Recent activities broadened this focus to multifunctional materials, supercapacitors, fuel cells, regenerable CO2 absorbers, electromagnetic shielding, radiation dosimetry and thermal management systems of interest for human space flight. Preliminary tests indicate improvement of performance in most of these applications because of the large surface area as well as high electrical and thermal conductivity exhibited by SWCNTs.

References:


Contact: s.arepalli@jsc.nasa.gov ; 281-483-5910
Carbon Nanotube Activities at NASA-Johnson Space Center

Sivaram Arepalli
ERC Inc./NASA-Johnson Space Center Houston, TX 77058

Central Michigan University, Mount Pleasant, MI
April 29, 2005
What are Carbon Nanotubes?

Allotropes of Carbon—Graphite, Diamond, C_{60}, C_{million}, ⋯

Nanotubes—Multiwall and Single wall (MWNT and SWNT)

Properties

Mechanical—handle large strains
Electrical—Metallic, semiconducting
Thermal—Anisotropic conduction
Misc.—Electron emission and large surface area

New Organic chemistry with this new form of Chemistry

Functional Groups attached to ends or sides to modify and enhance the SWNT properties and host matrices
Possibility of Nanosensors and multifunctional materials
Why Single Wall Carbon Nanotubes?

Mechanical Properties
- much stronger/lighter than steel

Thermal Properties
- high longitudinal conductivity (diamond)
- low transverse conductivity ($\alpha_0$)

Electrical Properties
- metallic, semiconducting tubes
- high conductivity (copper)
NASA Nanotechnology Roadmap

Increasing levels of system design and integration

Materials
- Single-walled nanotube fibers
- Nanotube composites
- Integral thermal/shape control
- Smart "skin" materials
- Biomimetic material systems

Electronics/computing
- Low-Power CNT electronic components
- Molecular computing/data storage
- Fault/radiation tolerant electronics
- Nano electronic "brain" for space Exploration
- Biological computing

Sensors and components
- In-space nanoprobe
- Nano flight system components
- Quantum navigation sensors
- Integrated nanosensor systems
- NEMS flight systems @ 1 μW
Nanotube Technology Development Areas

Six Key Areas for NASA

- Nanotube Production
  - NASA is currently funding a multi-year program of nanotube materials production and development at Rice University. However, numerous fundamental nanotube materials production needs were identified in this Roadmap, and the Rice Program should be tied to these needs.

- Modeling & Simulation
- Nanotube-based Materials
- Structural Applications
- Biological and Medical Applications
- Electronic & Mechanical Devices, Sensors, and Computing
JSC Nanotube Group Activities

1. Make targets for laser process from graphite powder and metal nitrates
2. Produce single-wall nanotubes using laser and arc processes
3. Nanotube purification
4. Nanotube characterization for purity, length, diameter
5. Composite fabrication
6. Composite testing and analysis
• Production and Growth Mechanisms
  – Production parameter study completed with variations in lasers, flow and furnace conditions
  • Importance of inner tube and sequencing of lasers
  – Photodissociation study of $C_{60}$: Source of excited state $C_2$
  – Growth mechanism study for laser ablation: Catalyst particles condense slower than carbon and carbon clusters break to provide additional carbon feed stock
    • Applied Physics A, Vol. 72, pp. 573-580 (May 2001)
  – Production of Isolated Individual SWNTs: Long lengths
JSC Nanotube Project Progress Details (Contd.)

- **SWNT Purification and Characterization**
  - Completed part 1 of the purification procedures
  - Completed a preliminary study of surface energy measurements for SWNTs during different stages of purification
  - Established protocols for purification of laser and HiPco materials as well as characterization of SWNT using TGA, SEM, TEM, Raman and UV-VIS
  - Trying to become a reliable source of SWNTs

**NASA/NIST Joint Workshop on Characterization**
• **SWNT Applications in Composites**
  
  – Completed a variety of processing techniques for the preparation of composites using thermosets and thermoplastics
  
  • Characterization of mechanical strength enhancements by DMA, Raman, and tensile tests
  
  – Utilized polarization study of Raman spectra to deduct load transfer to composites
  
  
  – Completed a study of mechanical response of SWNT ropes under tensile stress: Min. breaking strength of 50 GPa
  
AFM image of plate #1 exposed for 0.5 seconds, with inner tube and argon flowing at 100 sccm. a) Individual tube, 1.09 nm diameter. b) Individual tube, 1.17 nm diameter. c) Thin bundle, 3.28 nm diameter.
- Amount of ropes relative to individual nanotubes and thickness increases farther away from the target (more time to travel, more chance to bundle).

- Ropes and nanotubes deposit farther away from the target without inner tube.

- Relative amount of individual nanotubes is higher without inner tube (plume expands into larger volume, less chance to bundle up).
Purification Methods

- Acid reflux; cross flow filtration; centrifuging; solvent extraction and high temperature annealing
- Solvent Extraction; acid reflux; filtration and centrifuging followed by annealing
- Annealing followed by acid reflux; filtration and centrifuging
- Acid Reflux – Oxidizers like HNO$_3$, HCl, HF, H$_2$O$_2$  
  Helped to dissolve metals and amorphous carbon
- Cross Flow Filtration – Surfactants like TritonX  
  Separated the unbound impurities from pure nanotubes
- Solvent Extraction – Toluene, Benzene, DMF  
  Dissolved polyaromatics and fullerenes
- High Temperature Annealing in Argon – 500 to 1373 K  
  Removed volatile components and amorphous carbon
JSC Nanotube Characterization protocol

- Goal 1: To gather as much information as possible about specimen purity, metal content, dispersability and homogeneity.
- Goal 2: To minimize time and effort spent on characterization.
- Available tools: TGA, TEM (+EDS), SEM (+EDS), UV-Vis spectrometry, Raman spectroscopy.
- We have established a protocol which takes into account known inhomogeneity in nanotube specimens.
- Purity information: TGA, TEM, TEM-EDS, SEM, SEM-EDS, Raman
- Homogeneity information: TGA, TEM and SEM to some extent
- Thermal stability information: TGA
- Dispersability information: Sonication and UV-VIS test
Micro Characterization by Electron Microscopy: SEM and TEM

- **SEM:** Standardized sample mounting. Qualitative elemental analysis with EDX. Rough estimation of purity by comparing image areas.

- **TEM:** Need to wet the sample and dry it on the grid. Diameter distribution (tedious?). Surface imperfections and metallic contaminants. EDX for elemental analysis. Chirality and crystallinity by electron diffraction.
Macro Characterization by Optical Spectroscopy: Absorption (UV-VIS-NIR and IR), Fluorescence and Raman

**Absorption:** Inter band transitions in UV to NIR regions. Individual tubes vs. bundles. Effects of pH and solvents. Estimation of metals?

**Fluorescence:** Individual tubes, kinetics in solutions. Metal ligand interactions?

**Raman:** Small areas (micro?). Diameter distribution. Monitor amorphous carbon.
Other Analytical Tools: TGA, AFM, HPLC, NMR, GC-MS, ICP-MS, Microprobe.

- **TGA**: Burning of different types of carbon at different temperatures. Metal content.
- **AFM**: Individual tubes vs. bundles. Tube/rope lengths.
- **HPLC**: Small liquid samples. Purification tool. Fullerene/hydrocarbon content.
- **NMR**: Hydrocarbon content. Paramagnetic impurities.
- **GC-MS and ICP-MS**: Can be used for carbon and metal contents.
- **Microprobe**: Small areas for metal estimation. Need flat surface.
How do we go about estimating the purity of SWNTs at NASA-JSC?

1. Identify the extent of inhomogeneity.
2. Determine dispersability in selected solvents (DMF, toluene?)
3. Record SEM images.
4. Obtain Raman data.
5. Estimate fullerene and hydrocarbon content.
6. Record TEM images.
7. Estimate non-carbon content by TGA.
8. Identify metals by EDX.

NASA-JSC Protocol and Joint NASA / NIST Workshop
**Composite Fabrication and Testing**

**Types:** Thermosets, Thermoplastics, Elastomers, Ceramics

**Methods:** Injection Molding, Casting, Compression Molding, Die Casting and Laminating

**Samples:** Dog-bone, rectangular samples

**Testing:** Optical Microscope, Dynamic Mechanical Analysis, Raman, Tensile tests

**Characterization:** SEM, TEM, and Raman
Raman Characterization of Composites
Load Transfer in Nanotube Composites

- **New Tool** - Raman spectroscopy in combination with standard mechanical tests (four point bend) is very useful for testing SWNTs composites.

- Frequency of the tangential mode shifts with applied external compression stress.

- Allows determination of elastic properties of SWNTs/ropes embedded in composite - load transfer.

- **70% Load Transfer** (1%SWNT in epoxy)
Excellent Wetting of Nanotube Bundle in Epoxy

Why no big increase in strength?

- Bundles too large
- Curvature too high
- Wetting vs. bonding
Future Nanotube work at NASA-JSC

1. Modify laser production for improved yield.
2. Modify purification procedures to include variability of initial soft bake temperatures with samples.
3. Expand the JSC protocol to include optical microscopy for dispersion and TPO for identifying different types of carbon.
4. Establish techniques to monitor amorphous carbon.
5. Improve derivatization techniques to for selectivity of functional groups, their location and extent.
6. Improve methods to produce selective individual tubes and to disperse SWNT bundles.
7. Continue work on nanocomposites for mechanical, electrical and thermal aerospace applications.
Government Collaborations

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

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

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

Naval Research Lab.
- Composites (Imam)

NASA Langley Research Center
- Code R $-$ Production/purification (JSC) for use in SWNT composites (Siochi, Sutter)

Nat’l Renewable Energy Lab
- Purification (Heben, Dillon)

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

Oak Ridge Nat’l Lab.
- Thermal characterization (Wang, Dinwiddie)
University Collaborations

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

Rensselaer (RPI)
- Composites (Schadler)

Rice University
- Cooperative Agreement – Advanced
   Nanotechnology Mat'ls and Applications
   Yr. 4/5 (Smalley, Tour, Barrera, Margrave)
- Computational Mat'ls Sci. (Yakobson)
- Nanoshells (Halas)

University of Florida
- Isolated SWNTs (Rinzler)

Northwestern
- Mechanics/composites (Brinson)
- Nanotubes (Ruoff)

Univ. of Calif. - Davis
- Nanocrystalline Ceramics
  (Mukherjee)

LeTourneau Univ. (Clemson)
- Summer Faculty Fellow
  Nanotube growth process
  (DeBoer)

Clemson University
* Isolated SWNTs - STM (Carroll)

Univ. of Houston
- ISSO, year 3 of 3 – Raman
  Characterization (Iliev, Hadjieva)
- GSRP, year 1 of 2 – Polymer chem.,
  dispersion, composites (Mitchell,
  Krishnamoorti)

Univ. of Montpellier
- Arc process (Bernier)

Univ. of Texas - Tyler
- Summer Faculty Fellow - CFD
  of Laser process (Greendyke)
Team Members

Dr. Sivaram Arepalli
Dr. Rodrigo Devivar
Dr. Brad Files
Dr. Olga Gorelik
Dr. Brian Mayeaux
Dr. Pavel Nikolaev
Dr. Carl Scott
Dr. Erica Sullivan
Dr. Leonard Yowell

Mr. William Holmes
Mr. Lou Hulse
Mr. Jeremy Jacobs
Ms. Beatrice Santos

http://mmpitdpublie.jsc.nasa.gov/jscnano/

ACKNOWLEDGMENTS

- Dr. Rick Smalley and Dr. Bob Hauge of Rice University
- Dr. Victor Hadjiev of Univ. of Houston
- NASA-JSC Director’s Discretionary Funds
- Lockheed Martin ETAC contract
Carbon Nanotube Activities at NASA/JSC

Sivaram Arepalli

Thanks for your time!

Will be happy to answer a few questions!
Proton Exchange Membrane

- Hydrogen and oxygen are oxidized and reduced at the electrodes.
- e\(^{-}\) flow externally to create a current.
- H\(^{+}\) transverse the membrane.
- All recombine at the cathode to create water.
Requirements of a PEM Fuel Cell

**Electrodes**
- Electrodes must be conductive
- Electrodes should have high surface area
- Electrodes must be permeable to $O_2$ and $H_2$.

**Membranes**
- Membrane must be an insulator (electrical).
- Membrane must be permeable to $H^+$. 
- Membrane must be impermeable to $O_2$ and $H_2$. 
Membrane and Electrodes

- Electrodes have been made from slurry of carbon black and Pt black.
- To date, the membrane of choice is 3M’s Nafion.
Membrane and Electrodes

- Electrodes have been made from slurry of carbon black and Pt black.
- To date, the membrane of choice is 3M’s Nafion.

\[
\text{CF}_2\text{-}\text{CF}-\text{CF}_2\text{-}\text{CF}_2\text{-}O\text{-CF}_2\text{-CF}-\text{CF}_2\text{-}O\text{-CF}_2\text{-CF}_2\text{-}SO_3\text{-}H^+
\]
**SWNT for Fuel Cells**

**As Electrodes**

- SWNT are conductive.
- SWNT have high surface area.
- SWNT have longer conductive path than carbon black.
- H₂ mobility along the tube would be higher, possibly reducing the necessary Pt loading.

**As Membranes**

- Side walls of SWNT would have to be derivatized to become insulating.
- Derivatized SWNT are soluble in ordinary organic solvents.
- Negative charge would be delocalized so H⁺ removal would be enhanced.
Schedule of Work

**Electrodes**
- Make electrodes by filtration from low surface tension suspensions.
- Bake under inert atmosphere.
- Test surface area with BET surface analyzer.
- Test electrical conductivity.
- Test O\textsubscript{2} and H\textsubscript{2} diffusion.
- Impregnate with Pt salt and reduce in oven.

**Membranes**
- Derivatize (F\textsubscript{2} or oleum) SWNT.
- Suspend DSWNT in organic solvent.
- Make membranes
  - Filter from suspensions
  - Evaporate on PTFE
  - Dry with heat/pressure.
- Test electrical resistance across membrane.
- Test for O\textsubscript{2} and H\textsubscript{2} diffusion.
- Insert into standard fuel cell.
RCRS - Regenerable CO2 Removal Systems

- Plastic beads are coated with an amine
- Beads are packed in a compartment
- CO$_2$ reacts with amine and is retained in the chamber
- Applying vacuum and heating reverses the reaction, removing CO$_2$
Heat Exchange Problems with Current System

The reaction of Polyethylenimine with CO₂ is exothermic. During CO₂ removal, the system heats up, this reduces the efficiency of CO₂ removal from the atmosphere.

\[
\begin{align*}
R_1R_2NH + CO_2 & \leftrightarrow R_1R_2NH^+ CO_2^- \\
R_1R_2NH^+ CO_2^- + R_1R_2NH & \leftrightarrow \\
R_1R_2NH_2^+ + R_1R_2NCOO^- \\
\end{align*}
\]

Polyethylenimine

- Linear
- Branched

The reverse reaction is endothermic, which cools the system. Again efficiency of CO₂ removal is reduced. This time, the removal is from the amine substrate.
Thermal Transport is the Key to Efficient CO$_2$ Removal

- Nanotubes have a thermal conductance comparable to diamond along the axis.
- Nanotubes have large surface areas.
- Amines have been used to "hold" nanotubes to surfaces; i.e. amines stick to nanotubes.
- Multiwall nanotubes are available in large quantities.
- Multiwall nanotubes can be catalytically grown on multiple surfaces including meshes.
# Nanoscale Materials and Processes

## Characterization
- SWNT Load Transfer
- Single Fiber Diffusivity
- New Techniques

## Processing
- Purification
- Functionalization
- Dispersion
- Alignment

---

### Collaboration
- Academia, Industry, Government
- Applications for Human Spaceflight

---

<table>
<thead>
<tr>
<th>SUPPORT</th>
<th>APPLICATION</th>
<th>PARTNERS</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBIR Phase II</td>
<td>Ultracapacitors</td>
<td>EP, Glenn</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Rice (NCC 977)</td>
<td>Electrostatic Discharge Materials with Nanotubes</td>
<td>Rice, LaRC</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>Proton Exchange Membrane - PEM - Fuel Cells</td>
<td>EP, Glenn</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDDF - ES</td>
<td>Nanotube-Based Structural Composites</td>
<td>Rice, UHJ, LaRC</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>RCRS - Regenerable CO$_2$ Removal System</td>
<td>EC, Ames</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDDF - ES</td>
<td>Ceramic Nanofibers for Thermal Protection Materials</td>
<td>ES3, Ames, Glenn, USAF</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBIR Phase I</td>
<td>High Thermal Conductivity Fabric for Spacesuits</td>
<td>EC, Rice, ORNL</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDDF - ES</td>
<td>Radiation Resistance/Protection</td>
<td>NX, Rice, PV, LaRC, Ames</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>Active Thermal Control Systems for Space</td>
<td>EC</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDDF - ES</td>
<td>Nanoshells for Thermal Control Coatings</td>
<td>ES3, Nanospectra</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
What should we know about the Purity of the material?

Production Method and Source: Arc, CVD, HiPco, Laser, ....

Physical Appearance: Color, form, weight, homogeneity, ....

Solubility: Water, methanol, acetone, toluene, DMF, CS2, ....

-- Suspension, Flotation, Floculation

Dispersability: Visible transmission and changes with time

Electron Microscopy: SEM, TEM, EDX, XPS, ....

Spectroscopy: UV-VIS-NIR and IR absorption, Fluorescence and Raman

Other Analytical Tools: AFM, HPLC, NMR, GC-MS, Microprobe, ....
Considering Basic Composites Analysis

Typical composites construction is based on the volume fraction rule.

Note similarities in strain to failure. Usually, the matrix fails after the fiber.

However, Nanotubes have 5% elongation to failure.

Composite approaches throw away a significant contribution from the nanotubes.

Analysis with this approach would produce a material with a 3000% increase in strength, assuming ideal bonding and 1-D reinforcement.
Quick Calculation

Stiffness of SWNTs, \( E = 1 \times 10^{12} \text{ Pa} \)
E = stress/strain
If failure strain = 5%, failure stress = \( 1 \times 10^{12} \times 0.05 \)
\( = 50 \text{ GPa} \)
If material fails at 1%, stress in fibers = 10 GPa
Correction for 3-D randomness, \( 1/9 \times 10 \text{ Gpa (} \approx 1 \text{ GPa) } \)
If material has 1% SWNTs, \( 0.01 \times 1 \text{ Gpa} = 10 \text{ Mpa} \)
Epoxy tensile strength is 76 Mpa

Rule of Mixtures \( 10\text{MPa} + 76 \text{ Mpa} = 86 \text{ MPa} \)
Dispersion

- Both dispersion of ropes and individual tubes of SWNTs and epoxy
- Study compatibility with solvents
- Currently use acetone/toluene mixture for epoxy work
  - Toluene is used for compatibility with resin
  - Acetone is used to reduce evaporation time
- Need method to characterize dispersion
  - Light transmission, UV/VIS, Optical microscopy?
- Try water-soluble resins with wrapped tubes
- Work with surfactants?
LIF of C₂ in Plume

C₂ Energy Levels

\[ \text{P Branch} \]
\[ \text{Q Branch} \]
\[ \text{R Branch} \]
\[ \text{All Branches} \]

Intensity (arbitrary units)

Rotational Temperature (°K)

Open = Rotational Temperature
Filled = Bandhead Intensity

Intensity (arbitrary units)

Rotational Temperature (°K)

Open = Rotational Temperature
Filled = Bandhead Intensity

Wavelength (nm)

Intensity (arbitrary units)

Rotational Temperature (°K)

Open = Rotational Temperature
Filled = Bandhead Intensity

Wavelength (nm)
0.5% SWNT composite

![Graph showing Raman shift vs. surface strain](0.5%strfre.opj)