Abstract

Carbon Nanotubes for Human Space Flight

Carl D. Scott, Brad Files and Leonard Yowell
NASA Johnson Space Center, Houston, Texas

Single-wall carbon nanotubes offer the promise of a new class of revolutionary materials for space applications. The Carbon Nanotube Project at NASA Johnson Space Center has been actively researching this new technology by investigating nanotube production methods (arc, laser, and HiPCO) and gaining a comprehensive understanding of raw and purified material using a wide range of characterization techniques. After production and purification, single wall carbon nanotubes are processed into composites for the enhancement of mechanical, electrical, and thermal properties. This “cradle-to-grave” approach to nanotube composites has given our team unique insights into the impact of post-production processing and dispersion on the resulting material properties. We are applying our experience and lessons-learned to developing new approaches toward nanotube material characterization, structural composite fabrication, and are also making advances in developing thermal management materials and electrically conductive materials in various polymer-nanotube systems. Some initial work has also been conducted with the goal of using carbon nanotubes in the creation of new ceramic materials for high temperature applications in thermal protection systems. Human space flight applications such as advanced life support and fuel cell technologies are also being investigated. This discussion will focus on the variety of applications under investigation.
Carbon Nanotubes for Human Space Flight

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ES4/Materials and Processes Branch
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- Dr. Carl Scott
- Dr. Sivaram Arepalli
- Dr. Pavel Nikolaev
- Dr. Brian Mayeaux
- Dr. Brad Files
- Dr. Erica Sullivan
- William Holmes
- Beatrice Santos
- Dr. Olga Gorelik
- Dr. Rodrigo Devivar
Nanotube Ropes/Bundles
Why Single Wall Carbon Nanotubes?

**Mechanical Properties**
- much stronger/lighter than steel

**Thermal Properties**
- high longitudinal conductivity (diamond)
- low transverse conductivity ($C_{60}$)

**Electrical Properties**
- metallic, semiconducting tubes
- high conductivity (copper)

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**Stress-strain curve for SWNT ropes**
Rod Ruoff, Washington University, St. Louis & JSC

**Specific Modulus**
- Baseline Material, available today
- Best available, under development
- Emerging material, carbon nanotubes
- Long-term potential of CNT material

**Specific Strength**
- Carbon Nanotube Fiber Reinforced Polymer Composite
- Carbon Fiber Reinforced Polymer Composite
- Aluminum 2219

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Tensile Strength Comparison of Engineering Materials, GPa

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength (GPa)</th>
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<tr>
<td>Carbon Nanotubes</td>
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<tr>
<td>Carbon Fiber</td>
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<td>Aramid (Kevlar)</td>
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<td>Stainless Steel</td>
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Comparison of Engineering Materials: Carbon Nanotubes vs. Steel

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**Carbon fiber**

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**Steel**

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**Baseline Material, available today**

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**Best available, under development**

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**Emerging material, carbon nanotubes**

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**Long-term potential of CNT material**

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NASA Nanotechnology Roadmap

CAPABILITY

Multi-Functional Materials

High Strength Materials (>10 GPa)

Reusable Launch Vehicle (20% less mass, 20% less noise)

Revolutionary Aircraft Concepts (30% less mass, 20% less emission, 25% increased range)

Autonomous Spacecraft (40% less mass)

Bio-Inspired Materials and Processes

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, s/c components

- In-space nanoprobe
- Nano flight system components
- Quantum navigation sensors
- Integrated nanosensor systems
- NEMS flight systems @ 1 µW
JSC Nanoscale Materials Approach

• **Growth and diagnostics**
  - Ensure a reliable source of nanotubes with controlled properties using diagnostics and modeling to understand and improve processes

• **Purification and chemistry**
  - Develop processing methods for nanotubes to enhance structural, thermal, electrical, and chemical properties

• **Characterization**
  - Develop and employ characterization techniques to examine nanotubes and nanoscale materials

• **Applications**
  - Conduct initial studies or sponsor development of applications of nanoscale materials

• **Collaboration**
  - Establish a scientific network of academic, industry, and government partners to leverage resources and disseminate knowledge
JSC Nanotube Materials Approach

1. Make targets for laser process from graphite powder and metal nitrates
2. Produce single-wall nanotubes using laser process
3. Nanotube purification
4. Nanotube Characterization for purity, length, diameter
5. Specimen fabrication (composites, etc.)
6. Testing and analysis
Pulsed Laser Vaporization – “Laser” Process

Graphite $\xrightarrow{\text{Co, Ni Catalysts}}$ fullerenes + SWNT + impurities

4000-5000 K argon

Batch process
- 1g/day.
- Large diameters (~1-4nm)

furnace at 1200° Celsius

argon gas

neodymium-yttrium-aluminum-garnet laser

water-cooled copper collector

nanotube “felt” growing along tip of collector

graphite target
Growth and Diagnostics

Measurements of nanotube lengths as produced

- Nanotube length is extremely important for stress transfer in composite materials.
- Impossible to determine lengths of individual nanotubes from conventional TEM, SEM or AFM images because they bundle
- Processing (purification, sonication) seems to cut tubes
- Measured tensile strength (Ruoff) indicates long tubes
- Individual tubes longer than \(10 \mu m\) are required for strong ropes (Yakobson)

Our observation:
- We see very long \((\geq 20 \mu m)\) individual tubes and thin bundles

NASA Growth Mechanism Workshop

High Pressure CO (HiPCO) Process

CO + CO → Fe, Ni Catalysts → CO₂ + SWNT + impurities

900-1200°C
10-40 atm

Continuous process
10-100's g/day
Small diameters (0.7 nm)
- Company spin-off (CNI)

Rice Univ. → Carbon Nanotechnologies, Inc.
& NASA
Improved Production Capability

• **Growth and Production**
  - Ensure a reliable source of nanotubes with controlled properties using diagnostics and modeling to understand and improve processes

• **Laser Ablation Simulations and Diagnostics**
  - Summer Faculty Fellow Program
  - In-situ measurements of process parameters
  - Computational Fluid Dynamics Simulations
    - Collaboration with Dr. Robert Greendyke at UT-Tyler

• **Arc Process Diagnostics and Simulations**
  - Collaboration with Dr. Samir Farhat at University of Paris 13
Purification/Chemistry and Characterization

Purification techniques for HiPCO and Laser produced nanotubes

JSC

1. Rinse in H2O
   2. Reflux in CH3COOH
   3. Reflux in 7M HCl
   4. Reflux in conc. HCl
   5. Reflux in TNO2 at 100K

Rice

1. Soak sample in C360 (N)
   2. Stirring in conc. HCl for 265 hrs
   3. Repeated wash until pH 7
   4. Reflux in TNO3 at 100C

- Use {**standard characterization protocol**} to evaluate purified nanotube material and assess...
  - PURITY
  - HOMOGENEITY
  - THERMAL STABILITY
  - DISPERSABILITY

-> Techniques – TGA, SEM/TEM (+EDS), Raman, UV/Vis

Joint NASA / NIST Workshop – May 27-29, 2003
Characterization
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)
## Nanoscale Materials and Processes

### Applications for Human Spaceflight

<table>
<thead>
<tr>
<th>SUPPORT</th>
<th>APPLICATION</th>
<th>PARTNERS</th>
<th>TRL</th>
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<tr>
<td>SBIR Phase II</td>
<td>Ultracapacitors</td>
<td>EP, Glenn</td>
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<td>Nanotube-Based Structural Composites</td>
<td>Rice, UH, LaRC</td>
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<td>RCRS - Regenerable CO₂ Removal System</td>
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<td>Nanoshells for Thermal Control Coatings</td>
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Structural Composites
Nanotube Impact on Vehicle Scale

Baseline polymer composite structures and tanks

- 81% scale by length
  Nanotubes in polymer matrix
  Replace body, wing structures and propellant tanks

- 77% scale by length
  Nanotubes in aluminum matrix
  Replace body, wing structures and propellant tanks
High Thermal Conductivity Fabric for Spacesuits

- Nylon Spandex/SWNT fabric improves crew member’s thermal comfort
- Increased heat transfer rate from astronaut to sublimator

- SWNT thermal properties are extremely anisotropic; heat x-fer is high along length
- SWNT conductivity is comparable to that of diamond (2150 W/m-K)
Thermal Protection System (TPS) Materials

- **Next Generation Tiles**
  - Optimization of thermal properties at low, intermediate, and high temperatures allows TPS weight to be minimized, and improves vehicle performance.

- **Ceramic Nanofibers**
  - VGCF/SWNT templating via sol-gel processing
Ceramic Nanofibers for Thermal Protection Materials

Current LI-2200 Shuttle Tile
Solid Fibers
1-5μm (1000-5000nm)

Proposed
Hollow Fibers
0.1-0.3 μm (100-300nm)
Based on Carbon Nanofibers

Same Magnification - 5,000X

Proposed
Hollow Fibers
0.01-0.05 μm (10-50nm)
Based on Carbon Nanotube Ropes
NanosHELLS FOR THERMAL CONTROL COATINGS

- 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 absorptivity and high emittance

Courtesy of NanoSpectra
Proton Exchange Membrane (PEM) Fuel Cell

Electrodes
Catalyst Support Layer

Proton Exchange Membrane

Thermal Management Materials (High k)

Water Management (wicking)

Prevents the hydrogen and oxygen from mixing.

Transfers protons (H\(^+\)) from Anode to Cathode.

Electrons travel from Anode to Cathode through external load.

Anode (Catalytic Electrode)
\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

Cathode (Catalytic Electrode)
\[ 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \]

Overall Reaction:
\[ 2H_2 + O_2 \rightarrow 2H_2O \]
“CO$_2$ Scrubber”
RCRS – Regenerable CO$_2$ Removal System

- High surface area beads coated with amine-based chemical adsorbant
- When system is opened to space, material gets cold and not enough CO$_2$ is removed
- When CO$_2$ is adsorbed, material heats up, thereby limiting the amount of adsorption
- Need for new material: high surface area, improved thermal conductivity, ability to be coated with amine system
- Proposal currently in to the SLI program for funding for a NASA-led activity, as part of a larger proposal on RCRS
  - Carbon Foam Subscale Bed
  - Nanotube Array Bed (MWNT)
  - Carbon Whisker Bed
  - Amine Sheet Bed
Ultracapacitors

• Application
  – Use nanotubes as electrodes for energy storage, probably to be used in a hybrid system with batteries
• Current Collaborators
  – SBIR – ReyTech Corp., Inorganic Specialists
Electrostatic Discharge Materials with Nanotubes

- Applications
  - ESD packaging for humidity extremes
  - Light-weight conductive avionics racks and mounts
  - Oxygen and flame resistant ESD packaging

![Graph showing surface resistivity and concentration](image)

E.V. Barrera et al., Rice University
Active Thermal Control Systems for Space

- Four Basic Subsystems
  - **Heat Acquisition**
    - Advanced Cold-Plate Design
      - Carbon Fiber Composite
        (ThermalGraph Panels @ k=800W/m²K)
    - Carbon Fiber Velvet (Energy Sciences Lab.)
      - Thermal interface
  - **Heat Transport**
    - Heat transport fluids (BP Amoco, Mainstream Eng.)
      - Low freezing point
      - Non-toxic
      - High C_p (PPG)
  - Heat Rejection
  - Control and Monitoring
In-Space Manufacturing

Mixing aggregate and Masterbatching

Fibers 25-100 μm dia.

Pellets >3 cm

Wire ~2 mm dia. Feedstock

FDM Parts

Magnification 7X

E.V. Barrera et al., Rice University
Other Applications for Discussion

- EVA Lights
- Cold Cathodes
- Carbon-carbon
- Gas sensors
- Thermally conductive adhesives, greases
- Water purification
- Antennas
Government Collaborations

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

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

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

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

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

Naval Research Lab.
- Composites (Imam)

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

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. 5/5 (Smalley, Tour, Barrera, Margrave)
- Computational Mat’ls Sci. (Yakobson)
- Nanoshells (Halas)

Univ. of Florida
- Isolated SWNTs (Rinzler)

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

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

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

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

Clemson University
* Isolated SWNTS - STM (Carroll)

Univ. of Montpellier
- Arc process (Bernier)

Univ. of Texas - Tyler
- Summer Faculty Fellow – CFD
  of Laser process (Greendyke)
# Nanoscale Materials and Processes

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

## Growth/Production
- Laser and HiPCO
- Production and Diagnostics

## Processing
- Purification
- Functionalization
- Dispersion
- Alignment

## Collaboration
- Academia
- Industry
- Government

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<td>EF, Glenn</td>
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</table>
Composite Materials

I have issues...

• Dispersion
• Interface
• Morphology
• Orientation
• Processing
Interfaces

- If you compare a 1 nm fiber to a 1 micron fiber, you have a million times as many fibers for the same volume fraction,
- Interfaces are of interest in all composite materials
- In these nanocomposites the percentage of interfacial area is greatly multiplied
- Maybe all regions are interface
- Nanotube composites are very brittle
- Samples with nanotubes found to have more brittle characteristics than control samples.
Dispersion

TEM image of a bundle of single wall nanotubes

The carbon on the walls does not appear to be nanotubes. Is there also other carbon inside? What is the purity?
Morphology:
SEM of As-Produced Nanotube Ropes

How can you put this "Angel Hair" into a composite and expect to get strengthening?
Modulus of RTV Composite Materials

<table>
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<tr>
<th>Material</th>
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<td>Control</td>
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<tr>
<td>1% SIC Whiskers</td>
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<tr>
<td>1% Unpurified SWNT, Hand Mixed</td>
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<tr>
<td>5% Carbon Black-Ground</td>
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<tr>
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<td>5% Unpurified SWNT, Hand Mixed</td>
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<tr>
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<td>10% Unpurified SWNT, Mech Mixed</td>
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Nanotubes, Nanotube Composites and Applications for Human Spaceflight

Questions?
Single Wall Carbon Nanotube Composites

- Polymer/SWNT processing
- Bonding (functionalization)
- Dispersion of SWNTs/Bundles
- Alignment
Alignment?

E-beam Diffraction

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<th>Acc.V</th>
<th>Spot</th>
<th>Magn</th>
<th>Det</th>
<th>WD</th>
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SWNTs in Sol-Gel Zirconia