Measurement Challenges for Carbon Nanotube Material

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Abstract

The advances in large scale applications of carbon nanotubes demand a reliable supply of raw and processed materials. It is imperative to have a consistent quality control of these nanomaterials to distinguish material inconsistency from the modifications induced by processing of nanotubes for any application. NASA Johnson Space Center realized this need five years back and started a program to standardize the characterization methods. The JSC team conducted two workshops (2003 and 2005) in collaboration with NIST focusing on purity and dispersion measurement issues of carbon nanotubes [1]. In 2004, the NASA-JSC protocol was developed by combining analytical techniques of SEM, TEM, UV-VIS-NIR absorption, Raman, and TGA [2]. This protocol is routinely used by several researchers across the world as a first step in characterizing raw and purified carbon nanotubes. A suggested practice guide consisting of detailed chapters on TGA, Raman, electron microscopy and NIR absorption is in the final stages and is undergoing revisions with input from the nanotube community [3]. The possible addition of other techniques such as XPS, and ICP to the existing protocol will be presented. Recent activities at ANSI and ISO towards implementing these protocols as nanotube characterization standards will be discussed.

Ref.: 1) http://mmptdpublic.jsc.nasa.gov/jsccnano/
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OUTLINE

Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion

Study of fine variations in harvested material
  - Laser, arc and CVD production chambers

Additions to NASA-JSC protocol
  - Non-nanotube carbon and nanodispersion

Nanotube characterization standards

Future Work
QUESTIONS

Why do we need material quality assessment?

What do we have to know?

How do we perform the characterization?

How much time and money can we spend?

How many times do we need to do?

What else do we have to know about the production source, i.e. laser, arc, CVD, etc.?
Material Quality = Purity?

Why Do We Want to Know Nanotube Purity?

• Over the years, various manufacturers claimed purity anywhere from 50 to 90%. Do we trust these numbers? What are we buying?

• How consistent is NT material produced by the same manufacturer in different batches?

• What are implications of nanotube purity in applications?

• How does the purity affect stress transfer in composites, electrical and thermal conductivity, surface area, sidewall chemistry, dispersion properties, etc.?
SWCNT Measurement Challenges

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  - Laser, arc and CVD production chambers

Additions to NASA-JSC protocol
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Nanotube characterization standards

Future Work
How do We Perform Characterization?

**Macroscopic**
- Thermal Gravimetric Analysis (TGA)
- UV-Visible-Near Infrared (UV-Vis-NIR) Absorption
- NIR Fluorescence
- Inductively Coupled Plasma (ICP)
- Optical Microscopy
- Dynamic Light Scattering (DLS)
- X-ray Diffraction (XRD), SAXS, SANS
- Resistivity
- Surface Area (BET)
- Tensile Strength
- Thermal Conductivity

**Microscopic**
- Scanning Electron Microscopy (SEM)
- Energy Dispersive X-ray Analysis (EDX)
- Raman Spectroscopy
- X-ray Photoelectron Spectroscopy (XPS)

**Nanoscopic**
- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscopy (STM)

**Purity and Dispersion**
NASA-JSC Protocol for Purity and Dispersion*

- To be able to directly compare nanotube samples of different origin, purified by different techniques.

- To gather as much information as possible about specimen purity (non-nanotube carbon impurities and metal content), dispersability and homogeneity.

- To minimize time and effort spent on characterization.

- To optimize data collection to provide reliable assessment.

Available tools:

- Thermogravimetric analysis (TGA), (TA SDT 2960)
- Transmission electron microscopy (TEM) + EDS, (JEOL 2010 FX)
- Scanning electron microscopy (SEM) + EDS (Phillips XL40 FEG)
- Raman spectroscopy (Renishaw RM 1000)
- UV-Visible spectrometry (Perkin-Elmer Lambda 900)

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Material Variability with Production Source?

**Production and Collection**

**Arc Discharge Method**
- Wall Deposit
- Webs
- Collarette
- Cathode

**Pulsed Laser Vaporization**
- Collar Material 1.66%
- Sleeve Material 13.84%
- Filter Material 1.24%
- Inner Tube Material 6.61%
- Main Material 76.76%

**Arc Production Conditions:**
3.92%Ni:1%Y, Pressure: 506 Torr, Voltage: 38.2V, Current: 101.5A, Electrode Distance: 3 mm, Automated

**Laser Production Conditions:**
¾” diameter target, 1%Co:1%Ni, Pressure: 500T, Ar Flow Rate: 100 sccm, Pulse Separation: 50 ns, Power Density: 1.6J/cm², Oven Temperature: 1200 °C, Laser Sequence: Green-IR
Laser Run #171; Morphology

Collar

Sleeve

Main Material

Filter

Inner Flow Tube
Laser Run #171; Purity by EDX

Collar

Sleeve

Main Material

Filter

Inner Flow Tube
Harvested Laser Material: TGA Spectra

Inner Flow Tube: 6.51% 1.65% 13.84%
Collar: 76.76%
Sleeve: 1.24%
Main Material: 13.84%
Filter: 7.62%

* Indicates the percentage of material weight collected *
Laser Material: Raman Spectra (contd.)

\[ \omega_{RBM} = \alpha/d + b, \quad \alpha = \text{constant} = 223.5 \text{ cm}^{-1} \cdot \text{nm} \]
\[ b = \text{intertube interactions} = 12.5 \text{ cm}^{-1} \]
Harvested Laser Material: UV-Vis-NIR Spectra
### Laser Material Collection Variability Summary

#### MATERIAL

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>Inner</th>
<th>Collar</th>
<th>Sleeve</th>
<th>Main</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual Mass (%)</td>
<td>6.45%</td>
<td>13.98%</td>
<td>12.21%</td>
<td>14.26%</td>
<td>10.45%</td>
</tr>
<tr>
<td>Thermal Stability</td>
<td>Min 458.6 °C</td>
<td>Min 458.6 °C</td>
<td>Min 476.7 °C</td>
<td>Min 404.4 °C</td>
<td>Min 405.9 °C</td>
</tr>
<tr>
<td></td>
<td>Max 652.8 °C</td>
<td>Max 559.5 °C</td>
<td>Max 682.9 °C</td>
<td>Max 439.0 °C</td>
<td>Max 431.5 °C</td>
</tr>
<tr>
<td>Dispersion (%)</td>
<td>7.962%</td>
<td>13.31%</td>
<td>4.276%</td>
<td>3.821%</td>
<td>2.193%</td>
</tr>
<tr>
<td>D/G Ratios</td>
<td>0.288</td>
<td>0.090</td>
<td>0.047</td>
<td>0.094</td>
<td>0.124</td>
</tr>
<tr>
<td>D-Band Position cm(^{-1})</td>
<td>1285.45cm(^{-1})</td>
<td>1289.9cm(^{-1})</td>
<td>1287.87cm(^{-1})</td>
<td>1284.84cm(^{-1})</td>
<td>1283.17cm(^{-1})</td>
</tr>
<tr>
<td>Small Diameter %</td>
<td>8.02%</td>
<td>22.6%</td>
<td>8.17%</td>
<td>9.85%</td>
<td>27.5%</td>
</tr>
</tbody>
</table>
Laser Material Variability: Conclusions

- Downstream SWCNT material tends to have lower thermal stability
- TGA spectral shape similar for main and filter SWCNT material. Inner tube material has half the residual mass compared to other materials.
- Downstream material is less crystalline (?) and more fluffy (TGA and UV-Vis-NIR)
- Spectral features in UV-Vis-NIR data is directly proportional to distance from target
- Percent Absorption change is inversely proportional to distance from target
Variability Study of Harvested Arc Material

- Harvested Arc Material deposited on the cathode, collarette, webs and chamber wall.
- Characterized using JSC Protocol for SEM, TGA, UV-Vis and Raman
Harvested Arc Material: SEM and EDX

Cathode (JSC-A72.2)

Collarette (JSC-A72.1)

Webs (JSC-A72.3)

Wall Deposit (JSC-A72.4)

Resolution: 0.133 keV

Y or Si?
Harvested Arc Material: TGA Spectra

Possible causes for the variation: 1. Over-coating of metals  2. Tube diameters
Harvested Arc Material: Raman Spectra

Variability Study - Comparison of Harvested Arc Material (Normalized)

780 nm excitation

Scattering Intensity

Raman Shift (cm$^{-1}$)
Material deposited further away from electrodes have larger contribution of larger diameter tubes. 

\[ D_{\text{web}} > D_{\text{wall}} > D_{\text{col}} > D_{\text{cat}} \]

G-band agrees with diameter fractions – webs and wall deposit have higher fraction of larger diameters.
Harvested Arc Material: UV-Vis-NIR Spectra

**Harvested Arc Material: UV-Vis-NIR Spectra**

**Need to focus in on these regions**

- **Cathode**
- **Collarette**
- **Webs**
- **Wall Deposit**
# Arc Material Collection Variability Summary

## Arc Material:

<table>
<thead>
<tr>
<th>Properties</th>
<th>Cathode</th>
<th>Collarette</th>
<th>Webs</th>
<th>Wall Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual Mass (ave)</td>
<td>46.95%</td>
<td>46.60%</td>
<td>33.82%</td>
<td>29.61%</td>
</tr>
<tr>
<td>Min</td>
<td>458.8 °C</td>
<td>474.9 °C</td>
<td>356.4 °C</td>
<td>364.9 °C</td>
</tr>
<tr>
<td>Max</td>
<td>637.8 °C</td>
<td>646.6 °C</td>
<td>416.2 °C</td>
<td>418.8 °C</td>
</tr>
<tr>
<td>Thermal Stability (ave)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.5665%</td>
<td>1.595%</td>
<td>1.265%</td>
<td>0.114%</td>
</tr>
<tr>
<td>D/G Ratios</td>
<td>0.0337</td>
<td>0.1655</td>
<td>0.0873</td>
<td>0.0438</td>
</tr>
<tr>
<td>Small Diameter % (Raman)</td>
<td>20.9%</td>
<td>8.87%</td>
<td>5.39%</td>
<td>4.87%</td>
</tr>
<tr>
<td>Collection Region</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Arc Material Variability: Conclusions**

**TGA:**
Lower oxidation temps for material further from electrodes more likely due to some degree of over-coating.
Lower metal content observed inversely to distance from electrodes.

**Raman:**
D-band does not support TGA carbon impurity speculation.
RBM suggests smaller diameters more prevalent in cathode materials.
G-band may show more metallic features in cathode material, while more SC features in wall deposit.

**UV-Vis:**
Suppressed optical features support over-coating of tubes.
Stronger S22 transition in agreement with Raman results.
HiPco Material Variability Study - TGA

Front End Collection

Run #1
- Size: 2.9339 mg
- Temperature: 357.95°C → 419.85°C
- Derivative Weight: -0.2
- B: 28.35%
- T: 30.61%

Run #2
- Temperature: 364.30°C → 418.26°C
- Derivative Weight: -0.2
- B: 30.38%
- T: 31.17%

Run #3
- Temperature: 361.13°C → 418.26°C
- Derivative Weight: -0.2
- B: 29.05%
- T: 30.26%

Back End Collection

Run #1
- Temperature: 367.48°C → 389.70°C
- Derivative Weight: 2.0
- B: 20.42%
- T: 19.74%

Run #2
- Temperature: 367.48°C → 388.11°C
- Derivative Weight: 2.0
- B: 20.11%
- T: 19.64%

Run #3
- Temperature: 366.08°C → 389.93°C
- Derivative Weight: 2.0
- B: 21.65%
- T: 19.05%

Results:
1. Both Materials show good homogeneity from consistent TGA spectra
2. Back end material displays combustive behavior
3. Back end material has ~33% less non-carbon impurities
HiPco Material Variability Study: UV-Vis-NIR

**HiPco Variability Study - Front End Material**

Percent Absorption Change: 1.93%

**HiPco Variability Study - Back End Material**

Percent Absorption Change: 18.35%
SWCNT Measurement Challenges

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Nanotube characterization standards

Future Work
Non-nanotube Carbon by NIR Absorption

HiPco Variability Study - Back End Material

Wavelength (nm)

Absorbance

Wavenumbers (cm\(^{-1}\))

Absorbance

Percent Absorption Change: 18.35%

How do We Perform Characterization?

**Macroscopic**
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Purity and Dispersion
Macrodispersion and Nanodispersion
Optical Dispersion Analysis Protocol

Guidelines for a quantitative reproducible protocol:

• Follow guidelines for UV-Vis protocol and establish dispersion grade (A, B, or C).
• Once dispersion grade has been assigned, sonicate sample (0.1 mg/mL) for 1 h.
• After 1 h of sonication, allow sample to rest at room temperature for 1 h.
• Stir sample thoroughly and remove an aliquot (17uL)
  • A volume of 17 uL was found to be ideal for full coverage by a slide cover. This volume minimized the formation of vacuoles without excess spillage outside 22mm x 22mm area.
• Use the Optical Comparitor at 100x magnification equipped with a grid to count the particle distributions within an area.
• Count an area that represents the highest concentration of particles in the sample
• Use the ODA Protocol Table to determine the dispersion grade.
NIR Fluorescence for Nanodispersion

Chirality Determination

HiPco

Alcohol CVD

DOS

energy (eV)

semiconducting

S_{11}

S_{22}

(7,5)

(6,5)
Possible Additions to JSC Protocol

NIR Absorption for Purity Assessment

ODA, and NIR Fluorescence for Dispersion

AFM for Lengths and Diameters

E-Beam Diffraction, STM for Chirality

Electrical Conductivity

Thermal Conductivity

Mechanical Strength Measurements

TGA-IR/MS for Functional Group Assessment
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Future Work
Nanotube characterization standards

**NASA-NIST Collaboration**
- Purity and Dispersion Workshops 2003 and 2005
- Practice Guides on web page

**NASA-IEEE Collaboration**
- Development of IEEE-P1690 “Methods for the Characterization of Carbon Nanotubes Used as Additives in Bulk Materials”

**NASA-ANSI-ISO Collaboration under ISO-TC229 for Nanotechnology**
- Major Player in the US TAG for WG2 on Characterization
- Responsible for characterization standards of SWCNTs
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Future Work
Future Work

• Update characterization protocol for purity and dispersion of SWCNTs

• Identify and develop measurement standards for this characterization protocol
  SEM, TEM, TGA, Raman, UV-VIS-NIR Absorption, Optical Dispersion Analysis, NIR Fluorescence
Thanks for Your Attention
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http://mmptdpublic.jsc.nasa.gov/jscnano/

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