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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.?
What do We Really Like to Know?

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Purity</th>
<th>Dimensionality</th>
<th>Physical Properties</th>
<th>Chemical Interaction &amp; Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Shape</td>
<td>Density</td>
<td>Lengths</td>
<td>Thermal</td>
<td>Dispersion</td>
</tr>
<tr>
<td>Texture</td>
<td>Metal Impurity</td>
<td>Diameters</td>
<td>Electrical</td>
<td>Functionality</td>
</tr>
<tr>
<td>Color/Shade/Tint</td>
<td>Carbon Impurity</td>
<td>Chirality</td>
<td>Mechanical</td>
<td>Defects</td>
</tr>
<tr>
<td>Homogeneity</td>
<td>Other Impurities</td>
<td>Surface Area</td>
<td>Magnetic</td>
<td>Exfoliation</td>
</tr>
<tr>
<td>Surface Features</td>
<td>Residual Mass</td>
<td>Pore Size</td>
<td>Optical</td>
<td></td>
</tr>
<tr>
<td>Fiber Types</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Impurity Features</td>
<td></td>
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</tr>
</tbody>
</table>


## How do We Perform Characterization?

<table>
<thead>
<tr>
<th>Macroscopic</th>
<th>Microscopic</th>
<th>Nanoscopic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Gravimetric Analysis (TGA)</td>
<td>Scanning Electron Microscopy (SEM)</td>
<td>Transmission Electron Microscopy (TEM)</td>
</tr>
<tr>
<td>UV-Visible-Near Infrared (UV-Vis-NIR) Absorption</td>
<td>Energy Dispersive X-ray Analysis (EDX)</td>
<td>Atomic Force Microscopy (AFM)</td>
</tr>
<tr>
<td>NIR Fluorescence</td>
<td>Raman Spectroscopy</td>
<td>Scanning Tunneling Microscopy (STM)</td>
</tr>
<tr>
<td>Inductively Coupled Plasma (ICP)</td>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td></td>
</tr>
<tr>
<td>Optical Microscopy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic Light Scattering (DLS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray Diffraction (XRD), SAXS, SANS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface Area(BET)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td></td>
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</tr>
</tbody>
</table>

**Purity and Dispersion**
Our goals for Quality Assessment*

- 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)

How does the material vary with production source?

Production and Collection

Arc Discharge Method

Wall Deposit
Webs
Collarette
Cathode

Pulsed Laser Vaporization

Collar Material 1.66%
Sleeve Material 13.64%
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
TGA Harvesting Characterization

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

* Indicates the percentage of material weight collected *
Raman Spectroscopy Harvesting Characterization

Laser Variability - Normalized Spectra

![Graph showing normalized Raman spectra with labels for Inner, Collar, Sleeve, Main, and Filter.](image)

Scattering Intensity (arb. units)

Raman Shift (cm\(^{-1}\))
Raman Spectroscopy Harvesting Characterization

\[ \omega_{\text{RBM}} = \frac{\alpha}{d} + b, \quad \alpha = \text{constant} = 223.5 \text{ cm}^{-1} \cdot \text{nm} \]

\[ b = \text{intertube interactions} = 12.5 \text{ cm}^{-1} \]
Laser Run #171; Purity and Dispersion by UV-Vis-NIR Spectroscopy
## Laser Collection Variability Summary

### MATERIAL

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>Inner</th>
<th>Collar</th>
<th>Sleeve</th>
<th>Main</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Residual Mass</strong></td>
<td>6.45%</td>
<td>13.98%</td>
<td>12.21%</td>
<td>14.26%</td>
<td>10.45%</td>
</tr>
<tr>
<td><strong>Thermal Stability</strong></td>
<td><strong>Min</strong> 458.6 °C</td>
<td><strong>Min</strong> 458.6 °C</td>
<td><strong>Min</strong> 476.7 °C</td>
<td><strong>Min</strong> 404.4 °C</td>
<td><strong>Min</strong> 405.9 °C</td>
</tr>
<tr>
<td></td>
<td><strong>Max</strong> 652.8 °C</td>
<td><strong>Max</strong> 559.5 °C</td>
<td><strong>Max</strong> 682.9 °C</td>
<td><strong>Max</strong> 439.0 °C</td>
<td><strong>Max</strong> 431.5 °C</td>
</tr>
<tr>
<td><strong>Dispersion</strong></td>
<td>7.962%</td>
<td>13.31%</td>
<td>4.276%</td>
<td>3.821%</td>
<td>2.193%</td>
</tr>
<tr>
<td><strong>D/G Ratios</strong></td>
<td>0.288</td>
<td>0.090</td>
<td>0.047</td>
<td>0.094</td>
<td>0.124</td>
</tr>
<tr>
<td><strong>D-Band Position</strong></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><strong>Small Diameter %</strong></td>
<td>8.02%</td>
<td>22.6%</td>
<td>8.17%</td>
<td>9.85%</td>
<td>27.5%</td>
</tr>
</tbody>
</table>
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
Variability Study of Harvested Arc Material

Cathode (JSC-A72.2)  Collarette (JSC-A72.1)  Webs (JSC-A72.3)

Wall Deposit (JSC-A72.4)

Resolution: 0.133 keV

Y or Si?
Variability Study of Harvested Arc Material

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

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.
Variability Study of Harvested Arc Material

UV-VIS Dispersion Study: JSC-A72.2
JSC Arc unpurified-Harvesting Study, 120 min. Sonication, 0.6665% Change After 1 Hour

Need to focus in on these regions

UV-VIS Dispersion Study: JSC-A72.1
Arc unpurified, 15 min Sonication, 1.595% Change After 1 Hour

UV-VIS Dispersion Study: JSC-A72.3
JSC Arc unpurified-Harvesting Study, 30 min. Sonication, 1.265% Change After 1 Hour

UV-VIS Dispersion Study: JSC-A72.4
JSC Arc unpurified-Harvesting Study, 30 min. Sonication, 0.1114% Change After 1 Hour

Cathode

Collarette

Webs

Wall Deposit
## Arc Collection Variability Summary

### Arc Material:

<table>
<thead>
<tr>
<th>Properties</th>
<th>Collection Region</th>
<th>Cathode</th>
<th>Collarette</th>
<th>Webs</th>
<th>Wall Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Residual Mass (ave)</strong></td>
<td></td>
<td>46.95%</td>
<td>46.60%</td>
<td>33.82%</td>
<td>29.61%</td>
</tr>
<tr>
<td><strong>Thermal Stability (ave)</strong></td>
<td></td>
<td>Min 458.8 °C</td>
<td>Min 474.9 °C</td>
<td>Min 356.4 °C</td>
<td>Min 364.9 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 637.8 °C</td>
<td>Max 646.6 °C</td>
<td>Max 416.2 °C</td>
<td>Max 418.8 °C</td>
</tr>
<tr>
<td><strong>Dispersion</strong></td>
<td></td>
<td>0.6665%</td>
<td>1.595%</td>
<td>1.265%</td>
<td>0.114%</td>
</tr>
<tr>
<td><strong>D/G Ratios</strong></td>
<td></td>
<td>0.0337</td>
<td>0.1655</td>
<td>0.0873</td>
<td>0.0438</td>
</tr>
<tr>
<td><strong>Small Diameter % (Raman)</strong></td>
<td></td>
<td>20.9%</td>
<td>8.87%</td>
<td>5.39%</td>
<td>4.97%</td>
</tr>
</tbody>
</table>
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.
Thanks for Your Attention