Developing Carbon Nanotube Standards at NASA

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OUTLINE

Current state of reliability and uncertainty

NASA-JSC protocol for purity and dispersion

Applying JSC protocol to compare purification techniques

- **-Laser material**

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 repeat to gain statistics?

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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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)

* Ref: "NASA-JSC Protocol"; Carbon, Vol. 42, pp. 1783-1791 (2004)

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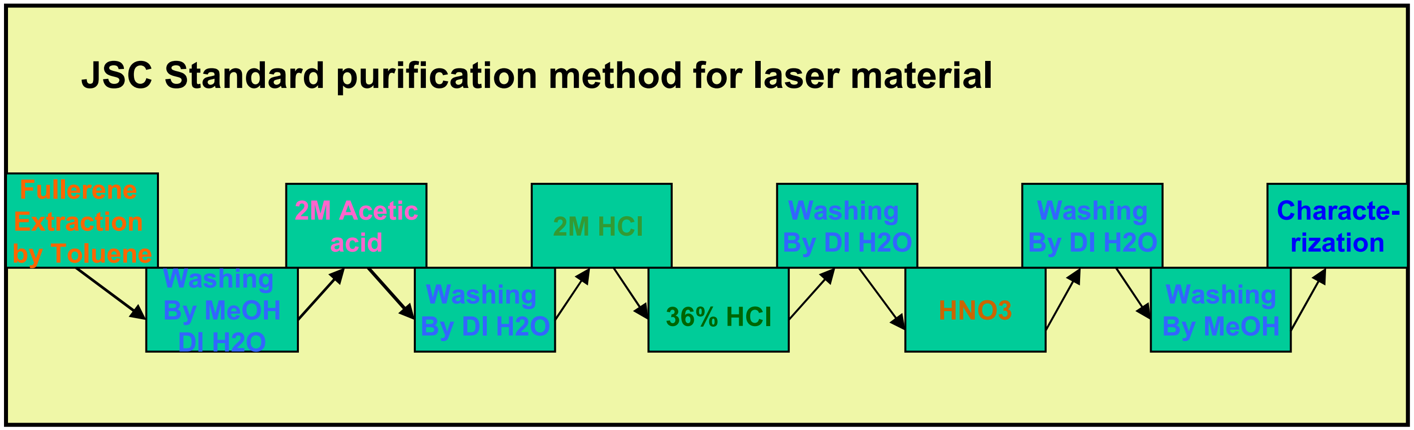
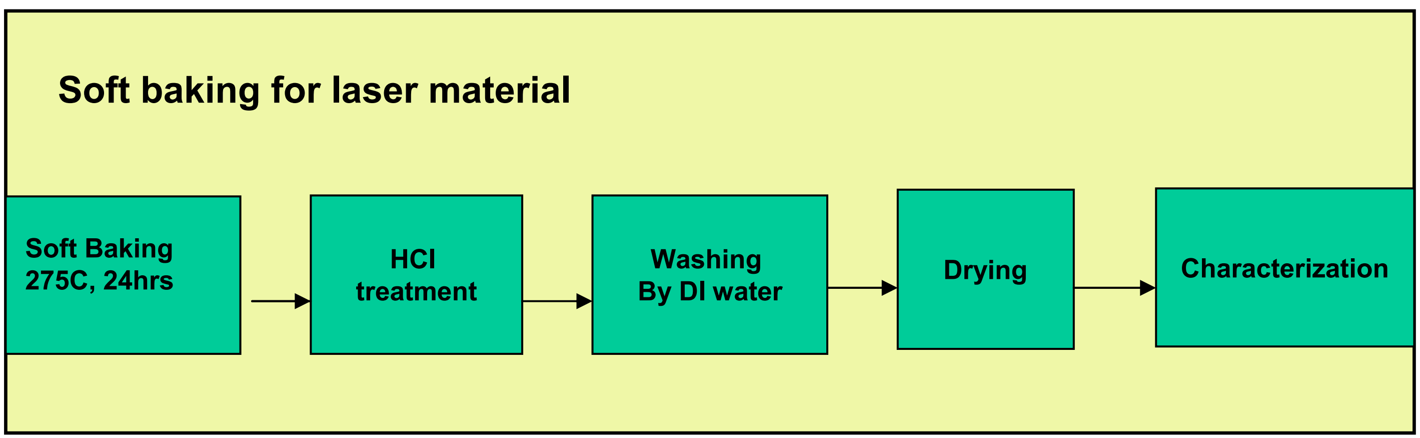
Applying JSC protocol:
Comparison of Two Purification Techniques

Same starting material: raw PLV SWCNT produced at JSC (6 samples)



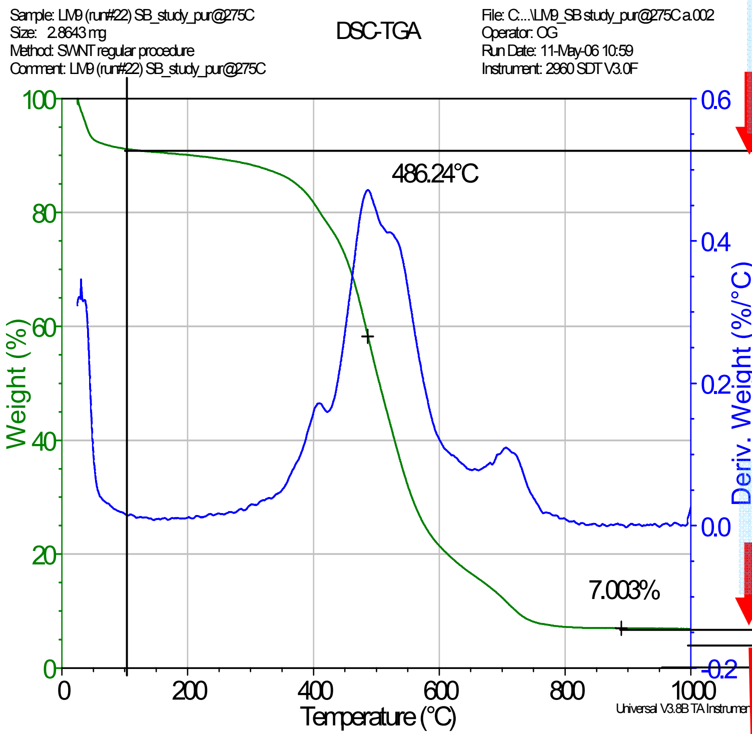
Laser standard purification: Typical batch size 5 g;
Multi-step process, takes ~3 weeks; 8 samples



Laser soft-bake purification: Typical batch size 1 g (so far);
Two-step process, takes <1 week; 7 samples

Soft-bake purification of single-walled carbon nanotubes produced by pulsed laser vaporization. *P. Nikolaev, et. al accepted for publication in JPhysChem*

Treatment of TGA / UV-Vis Data

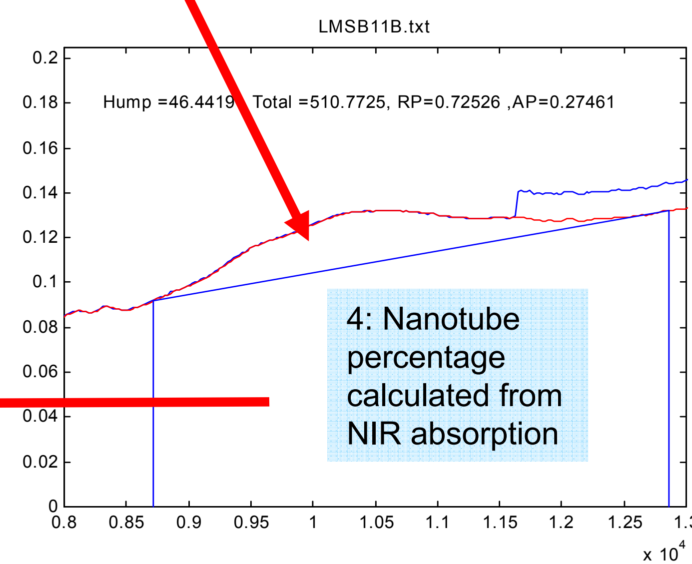


1: Water content taken out at 100°C

2: Metal oxides converted into pure metals

3: Total carbon calculated

M. E. Itkis, et al. Nano Lett, **3**, 309 (2003)



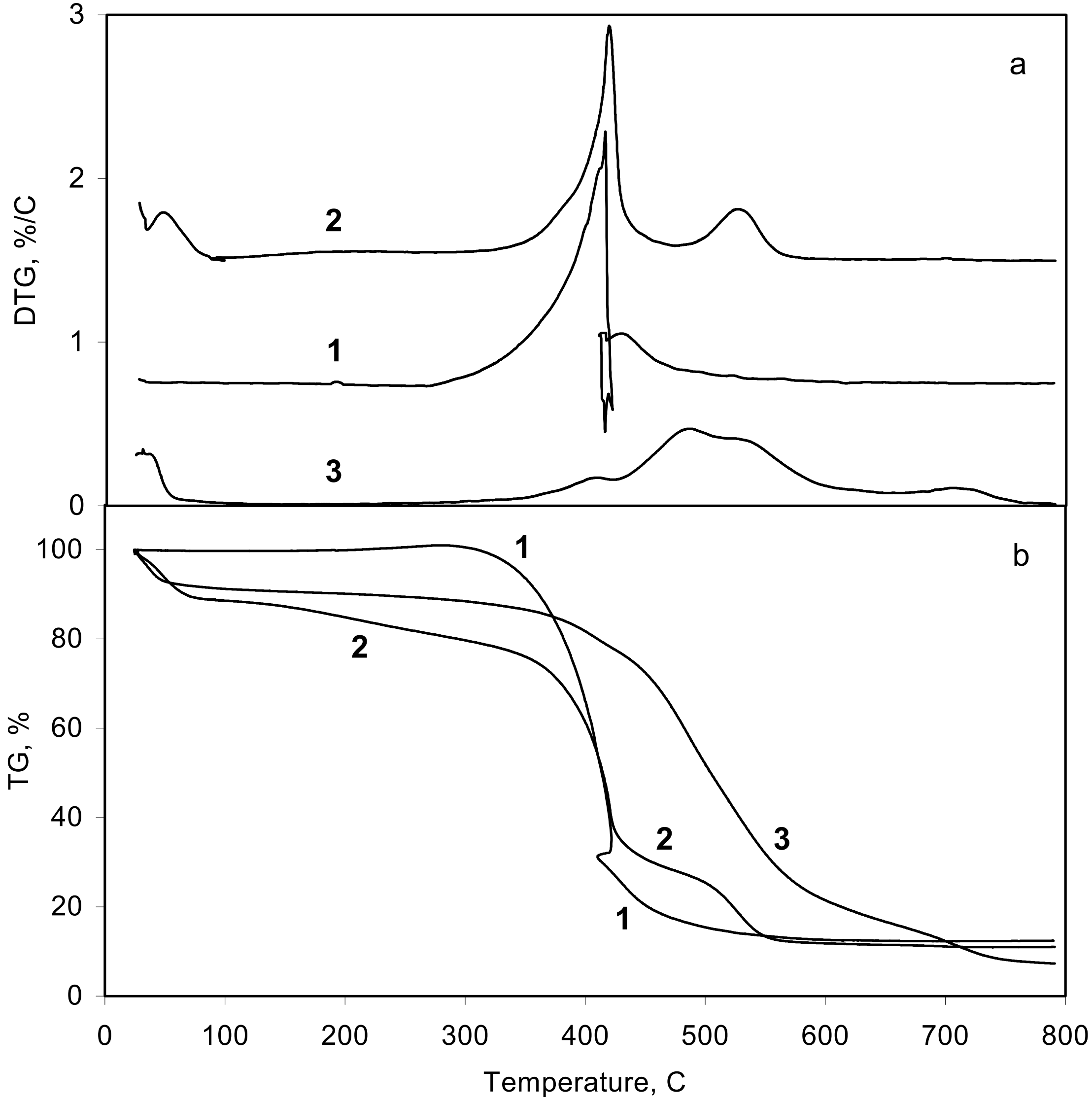
4: Nanotube percentage calculated from NIR absorption

5: Result:

Nanotube percentage in the sample (by weight)

Metal percentage in the sample (by weight)

Examples of TGA Data

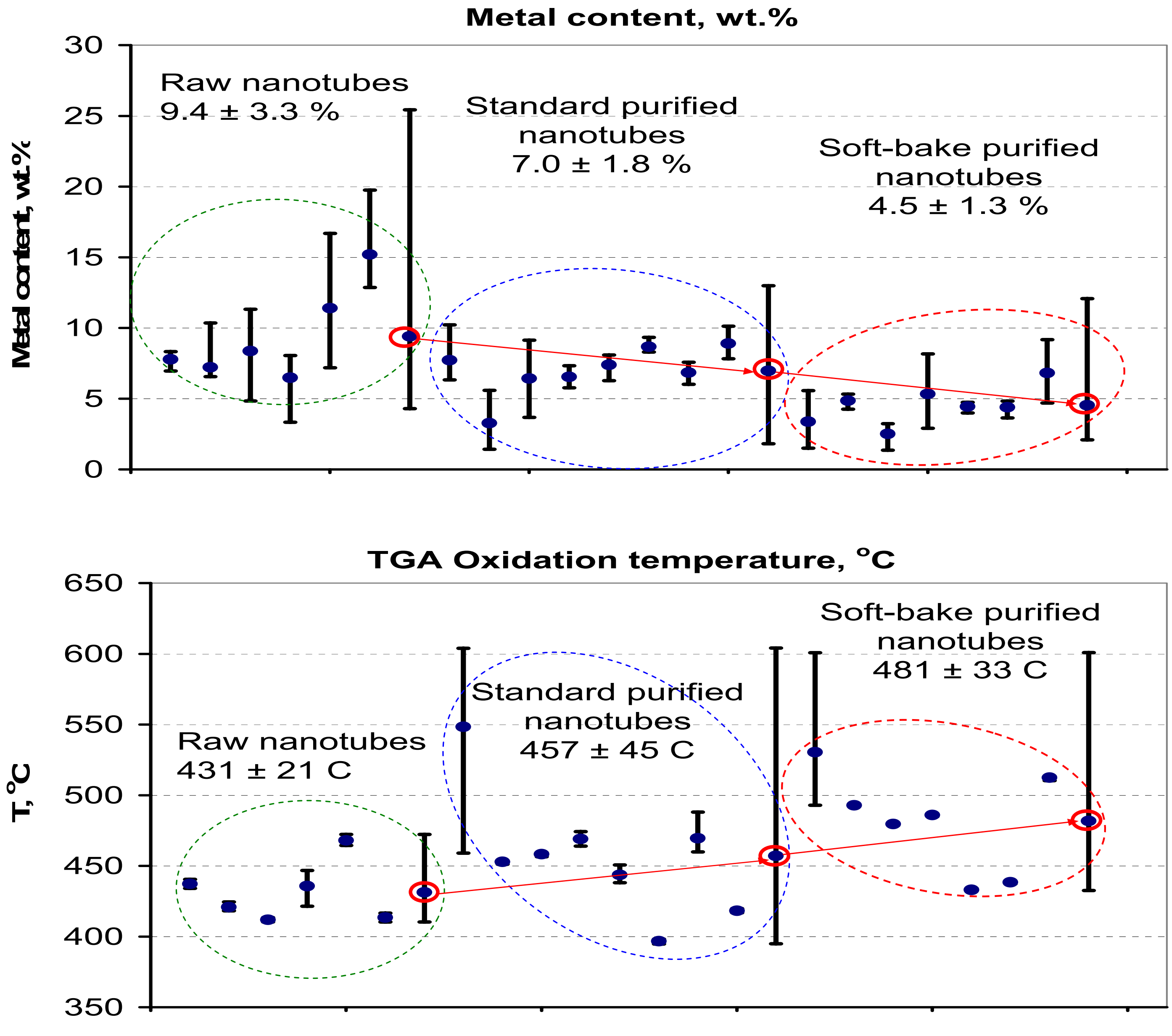


1 – raw PLV nanotubes

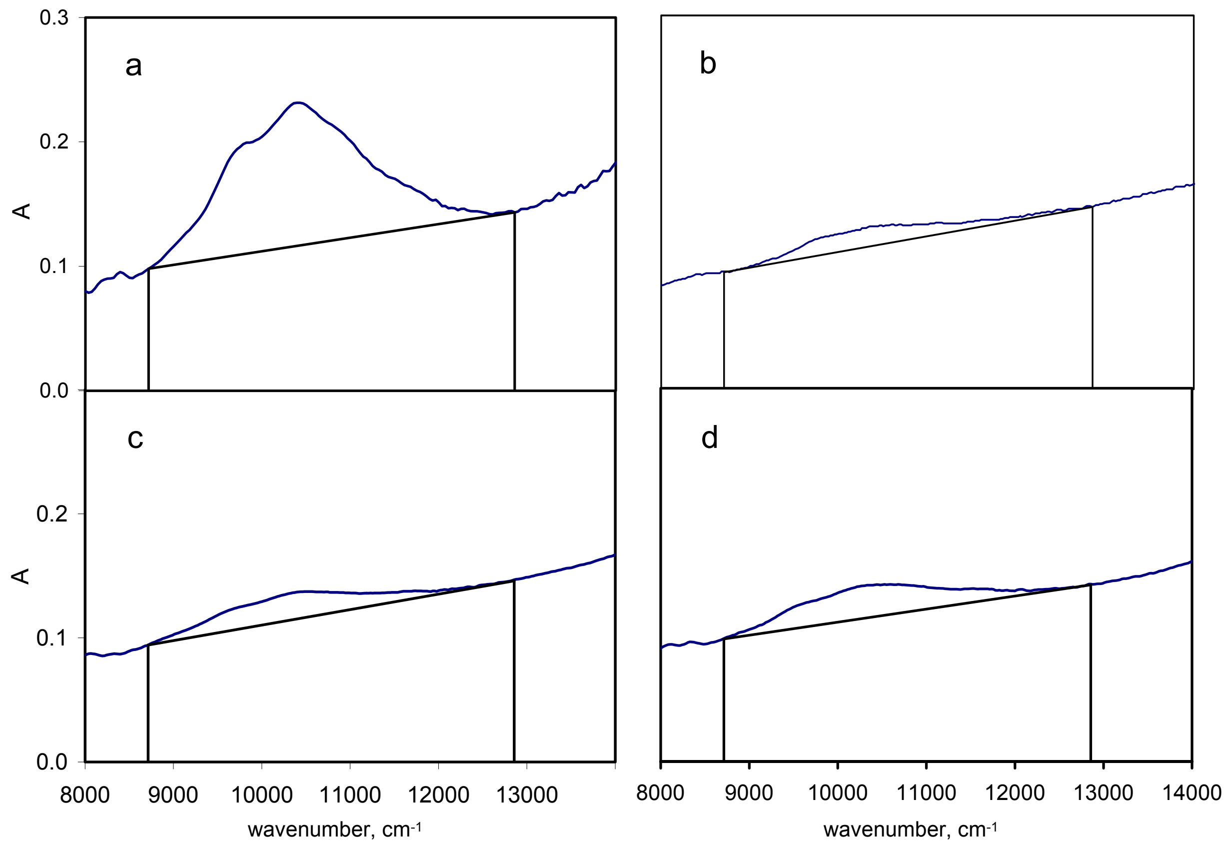
2 – standard purified PLV nanotubes

3 – soft-bake purified PLV nanotubes

TGA-derived Data for All Samples

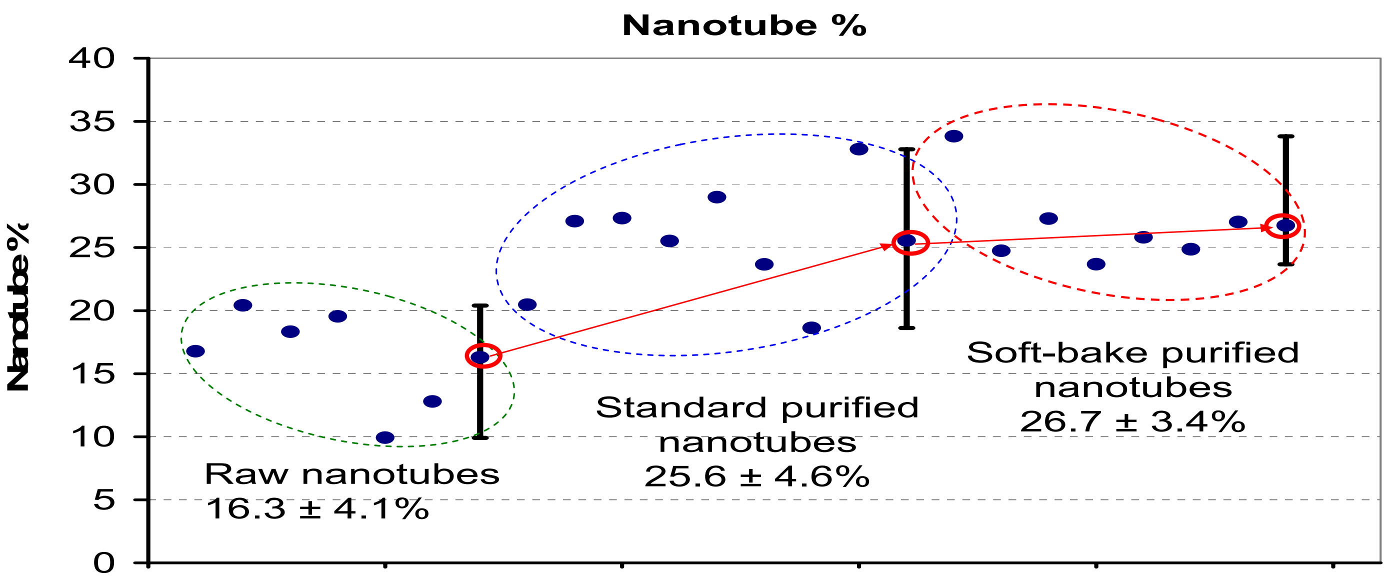


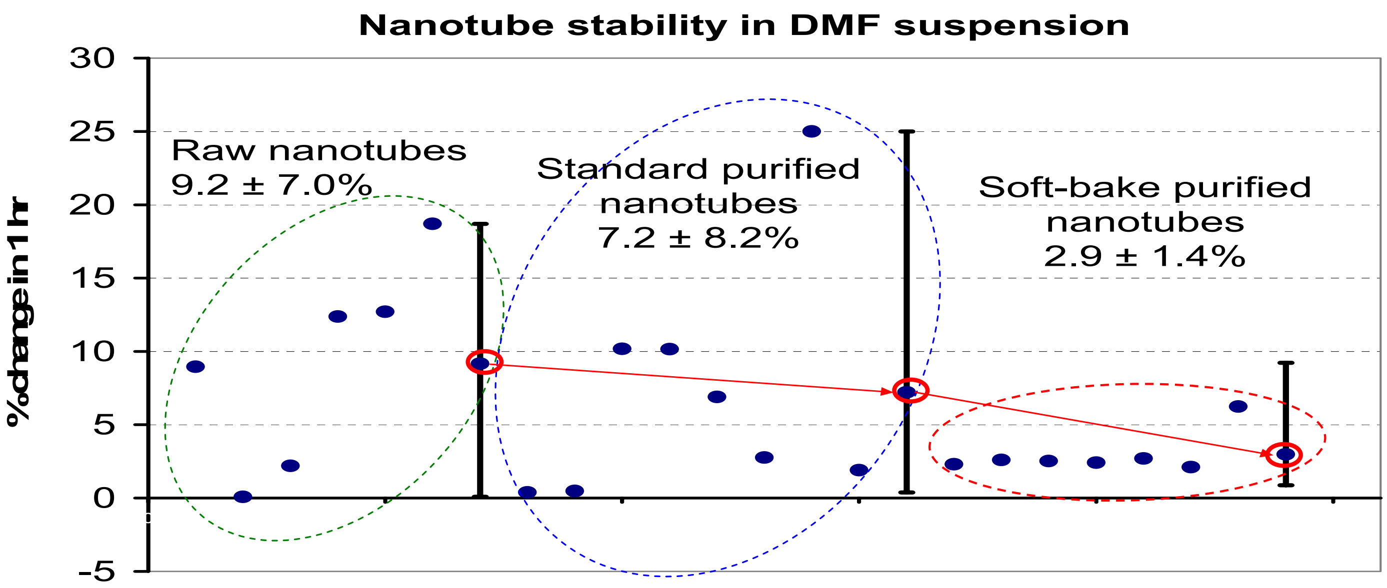
UV-Vis-NIR Absorption Spectra



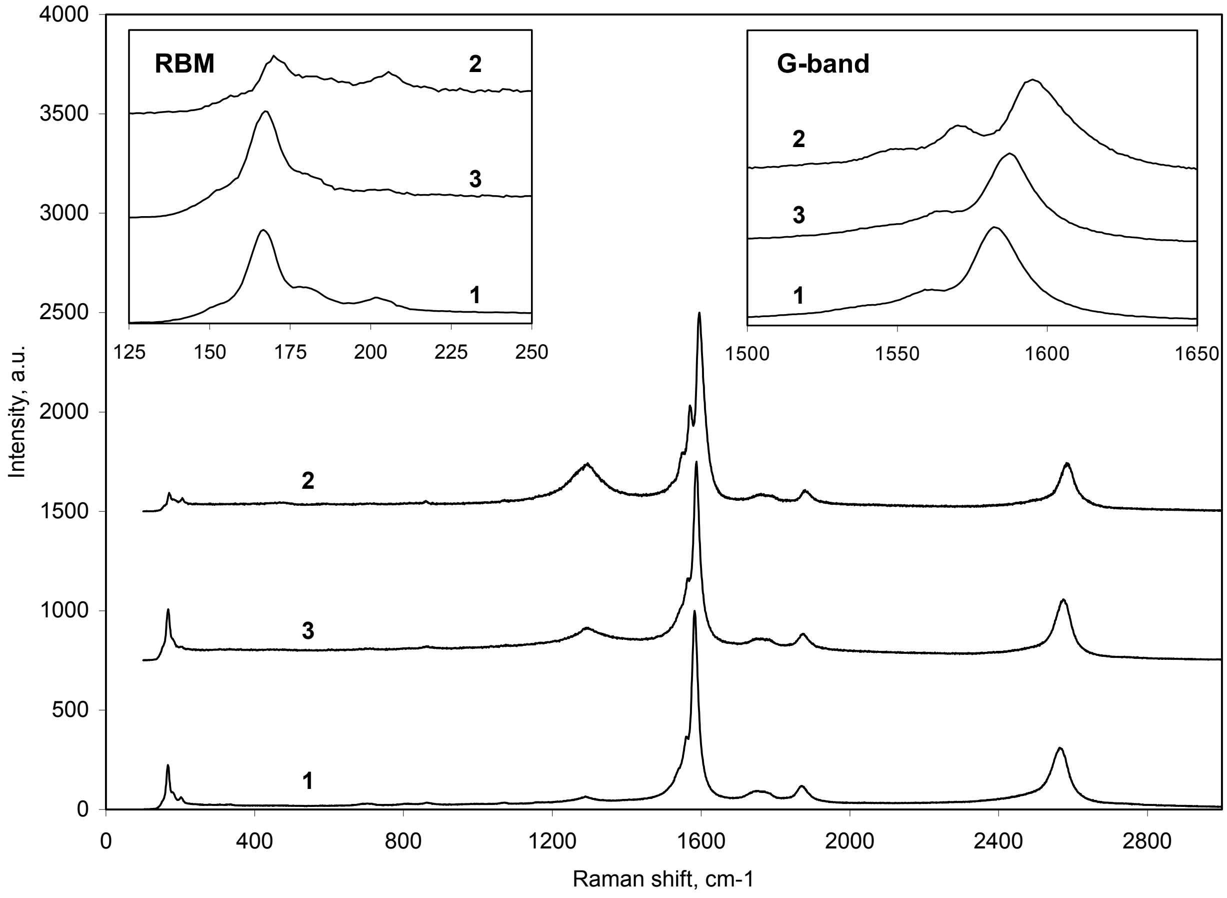
A – reference sample used for purity calculations.
B - raw PLV nanotubes
C – standard purified PLV nanotubes
D – soft-bake purified PLV nanotubes

"UV-Vis-NIR"-derived Data for All Samples





Examples of Raman Spectra



1 - raw PLV nanotubes

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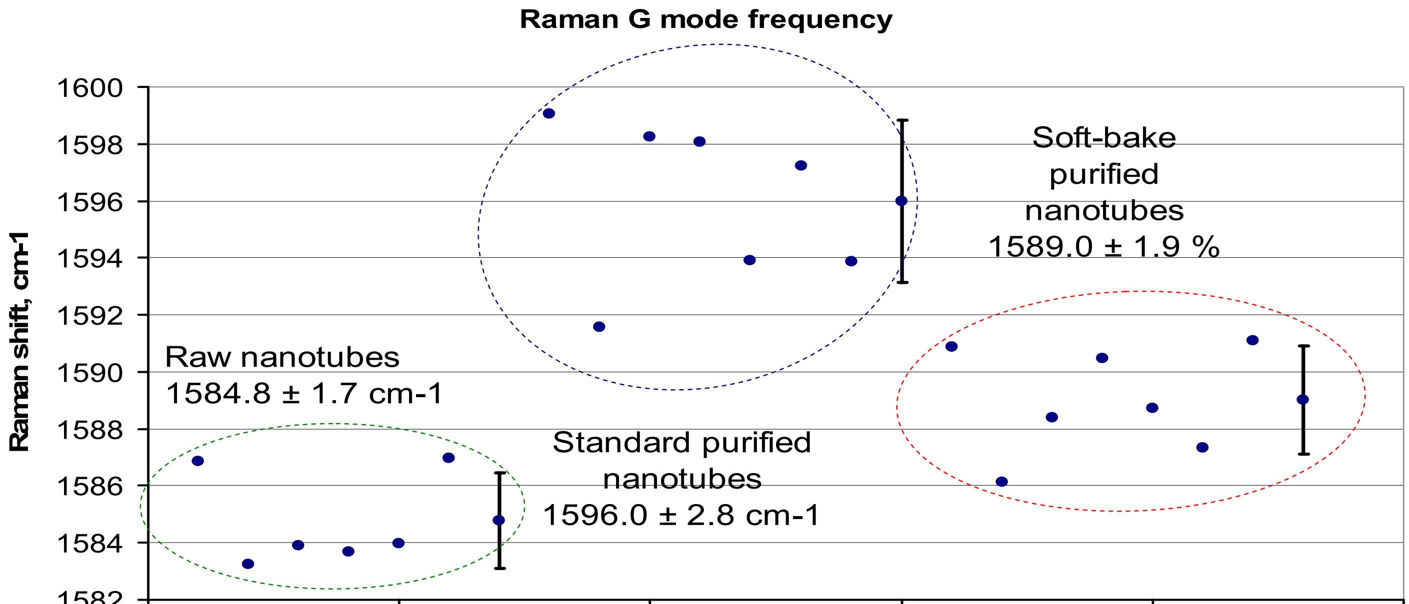
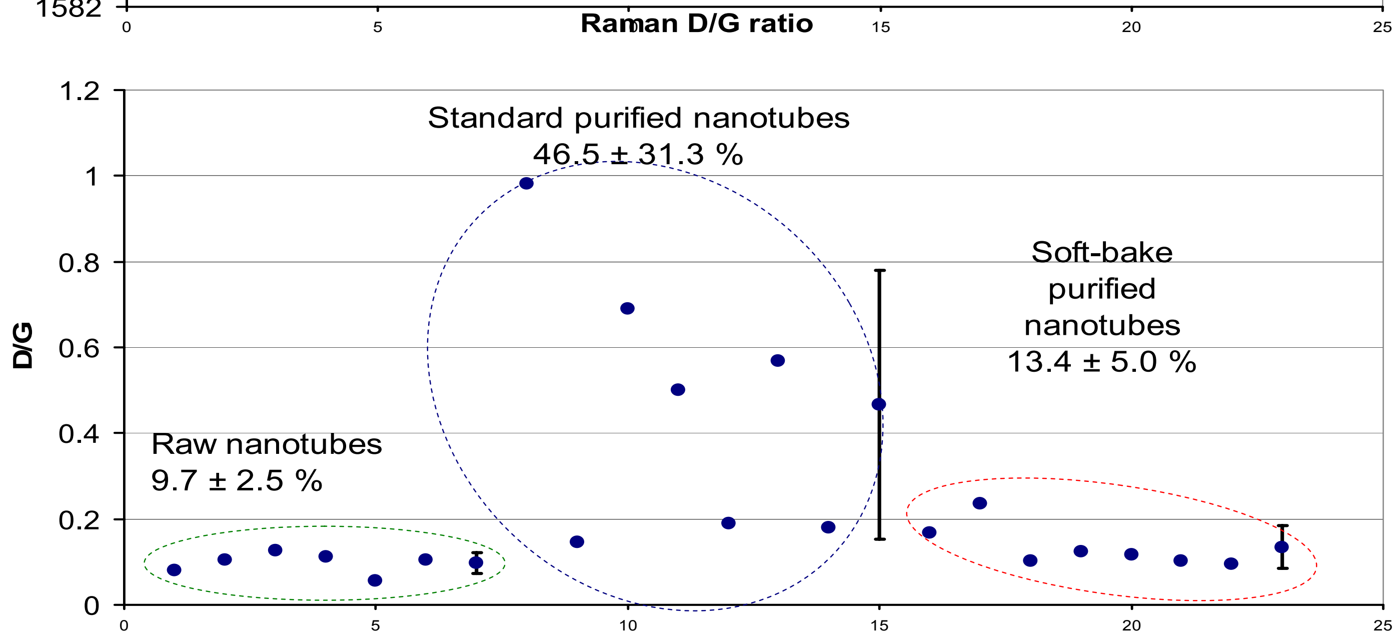
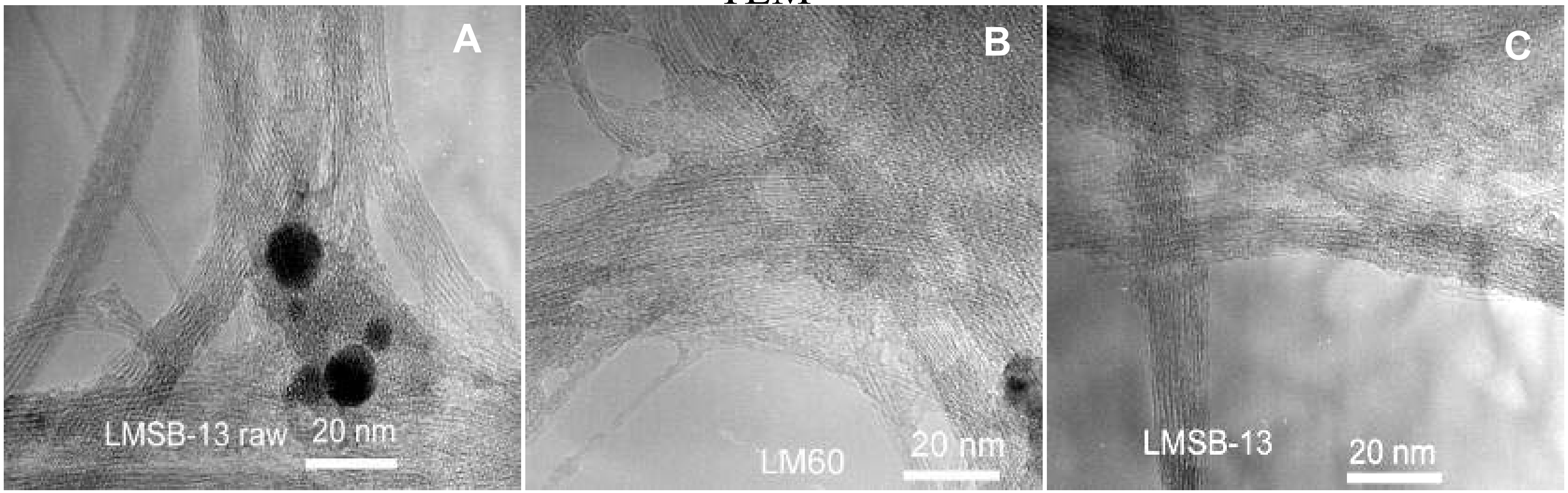
Raman Data for All Samples



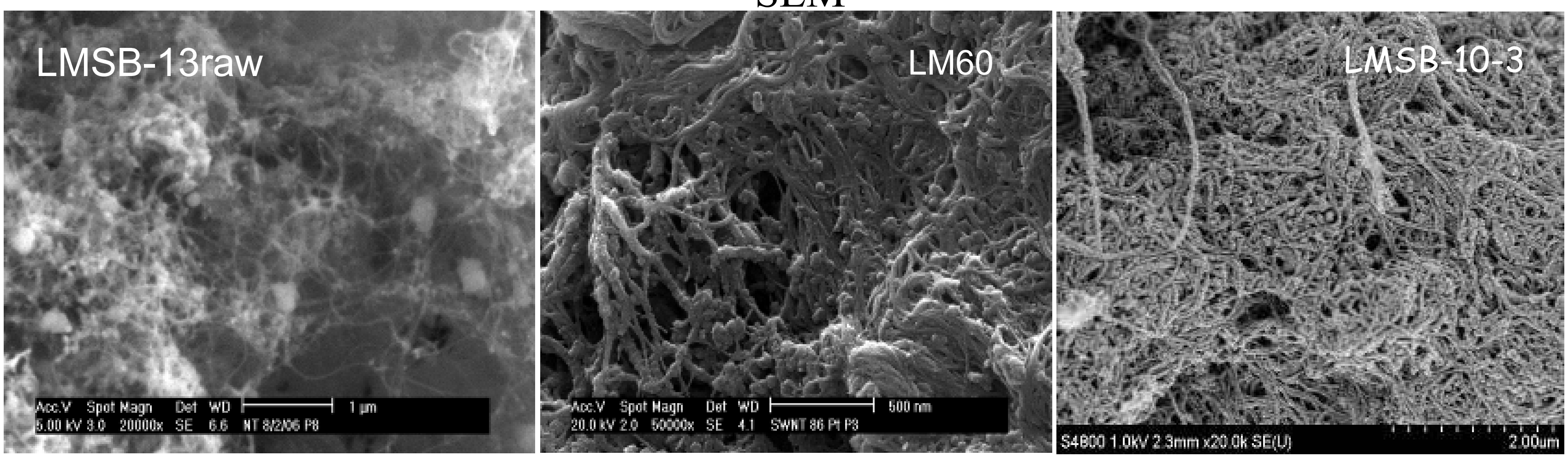


Examples of TEM and SEM Images

TEM



SEM



A - raw PLV nanotubes
B – standard purified PLV nanotubes
C – soft-bake purified PLV nanotubes

Averaged Data for All Samples

Sample	Raw material	Standard purified materials	Soft-bake purified materials
Metal content (M_r)	9.4 ± 3.3 %	7.0 ± 1.7 %	4.5 ± 1.4 %
Oxidation temp (T_o)	431 ± 21 ^oC	457 ± 45 ^oC	481 ± 33 ^oC
Nanotube content	16.3 ± 4.1 %	25.6 ± 4.6 %	26.7 ± 3.4 %
Dispersability	9.2 ± 7.0 %	7.2 ± 8.2 %	3.0 ± 1.4 %
Raman G-mode	1584.8 ± 1.7 cm^{-1}	1596.0 ± 2.8 cm^{-1}	1589.0 ± 1.9 cm^{-1}
Raman D/G	9.7 ± 2.5 %	43.3 ± 30.4 %	13.4 ± 5.1 %
Purification Yield	N/A	60.4 ± 8.5 %	50.2 ± 7.5 %

Data for All Samples

	Metal content, %	Oxidation temp, ºC	Nanotube content, %	Stability in DMF, %	Raman G-mode	Raman D/G
Raw samples						
1	7.8 ± 0.7	437.3 ± 3.2	16.8 ± 0.1	8.9	1586.8 ± 1.8	0.080 ± 0.021
2	7.2 ± 2.8	420.9 ± 3.3	20.4 ± 0.7	0.1	1583.2 ± 0.6	0.105 ± 0.061
3	8.4 ± 3.3	411.9 ± 1.6	18.3 ± 0.7	2.2	1583.9 ± 0.1	0.125 ± 0.079
4	6.5 ± 2.7	435.7 ± 13.0	19.5 ± 0.6	12.4	1583.7 ± 3.9	0.112 ± 0.055
5	11.4 ± 4.8	468.1 ± 3.9	9.9 ± 0.6	12.7	1583.9 ± 2.7	0.056 ± 0.019
6	15.2 ± 3.9	413.5 ± 3.2	12.8 ± 0.7	18.7	1586.9 ± 3.3	0.105 ± 0.044
Standard purified						
1	7.7 ± 2.2	548.4 ± 78.2	20.5 ± 0.5	0.4	1590.3 ± 3.2	0.208 ± 0.072
2	3.3 ± 2.1	452.9 ± 0.3	27.1 ± 0.6	0.5	1599.1 ± 0.1	0.982 ± 0.029
3	6.4 ± 2.7	458.3 ± 1.6	27.3 ± 0.8	10.2	1591.6 ± 1.5	0.146 ± 0.039
4	6.5 ± 1.1	469.1 ± 7.3	25.5 ± 0.3	10.1	1598.2 ± 2.9	0.691 ± 0.051
5	7.4 ± 1.0	443.6 ± 6.5	29.0 ± 0.3	6.9	1598.1 ± 2.4	0.500 ± 0.133
6	8.7 ± 0.6	396.8 ± 1.9	23.6 ± 0.2	2.8	1593.9 ± 0.5	0.190 ± 0.042
7	6.8 ± 0.8	469.6 ± 16.1	18.6 ± 0.2	25	1597.2 ± 0.4	0.567 ± 0.335
8	8.9 ± 1.1	418.3 ± 1.6	32.8 ± 0.4	1.9	1593.9 ± 0.4	0.180 ± 0.088
Soft-bake purified						
1	3.4 ± 2.0	530.4 ± 61.0	33.8 ± 0.7	2.3	1590.9 ± 0.8	0.167 ± 0.065
2	4.9 ± 0.5	492.8 ± 0.1	24.7 ± 0.1	2.6	1586.1 ± 4.6	0.235 ± 0.065
3	2.5 ± 1.0	479.6 ± 0.9	27.3 ± 0.3	2.5	1588.4 ± 1.7	0.102 ± 0.039
4	5.3 ± 2.6	486.0 ± 0.9	23.7 ± 0.7	2.4	1590.5 ± 1.3	0.124 ± 0.014
5	4.4 ± 0.4	433.1 ± 0.9	25.8 ± 0.1	2.7	1588.7 ± 1.3	0.116 ± 0.021
6	4.4 ± 0.7	438.4 ± 0.9	24.9 ± 0.2	2.1	1587.3 ± 4.2	0.101 ± 0.031
7	6.8 ± 2.2	512.4 ± 1.8	27.0 ± 0.7	6.2	1591.1 ± 0.5	0.095 ± 0.002

Conclusions

•Purity and yield of the standard and soft-bake purification procedures were monitored for several SWCNT samples

•Comparison with raw nanotubes properties

•It was demonstrated that PLV SWCNT can be successfully purified by a soft-baking technique

•Better removal of metal impurities

•Reduction in the required time and effort

•The JSC characterization protocol is a very useful tool for monitoring purification results in a consistent fashion

•A relatively large number of samples studied allowed us experimentally confirm improvements in the batch-to-batch reproducibility

•This approach, similar to a quality control system, may be useful in industrial scale-up of purification of carbon nanotubes

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→ Additions to NASA-JSC protocol
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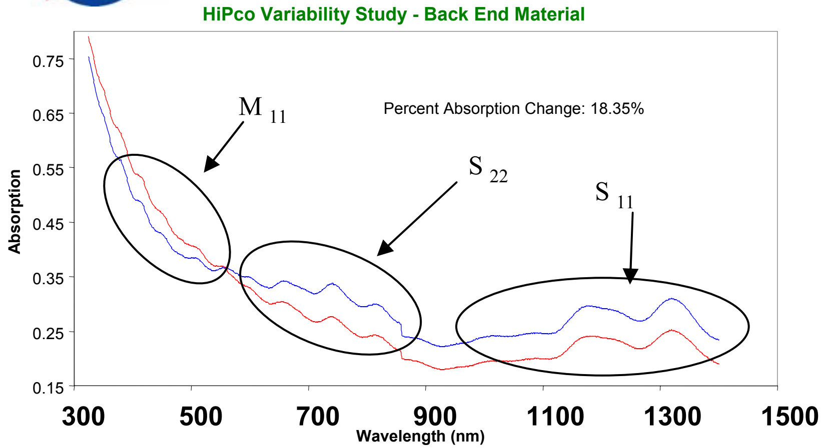
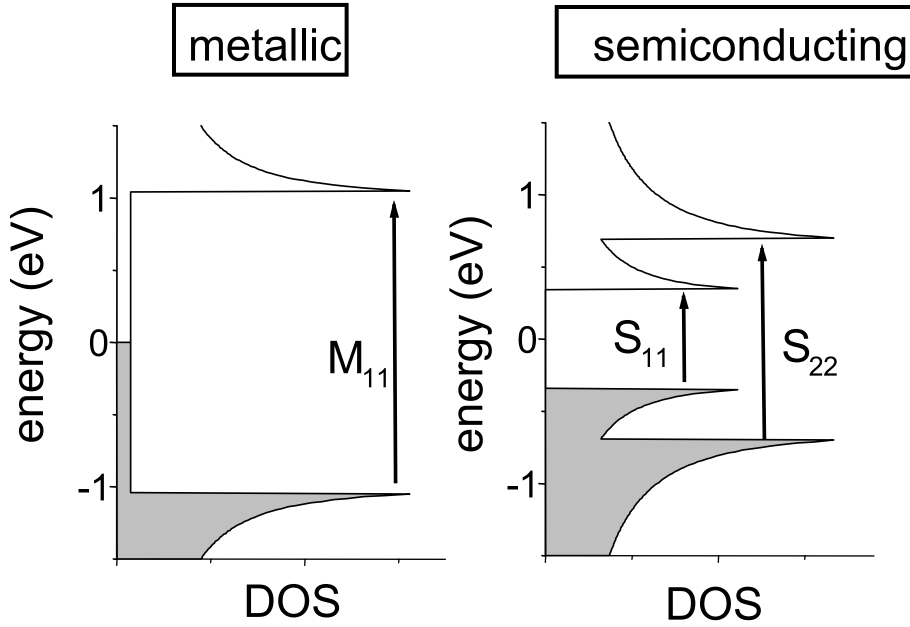
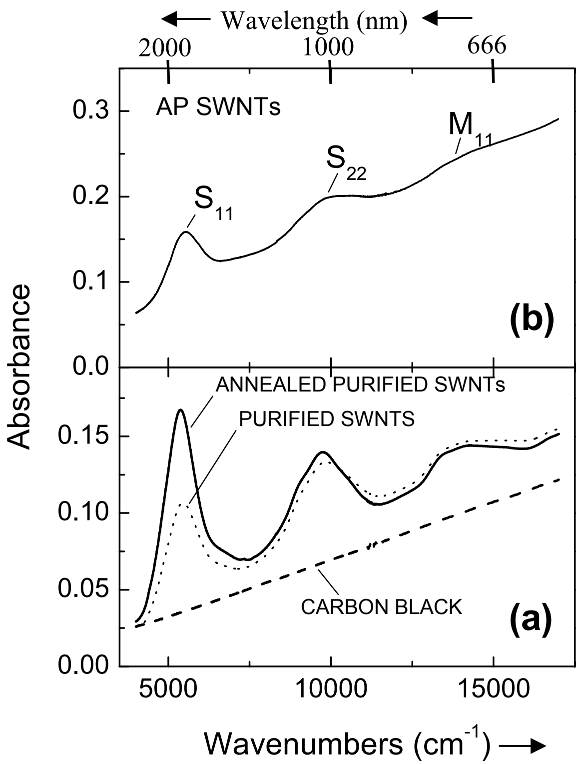
Nanotube characterization standards

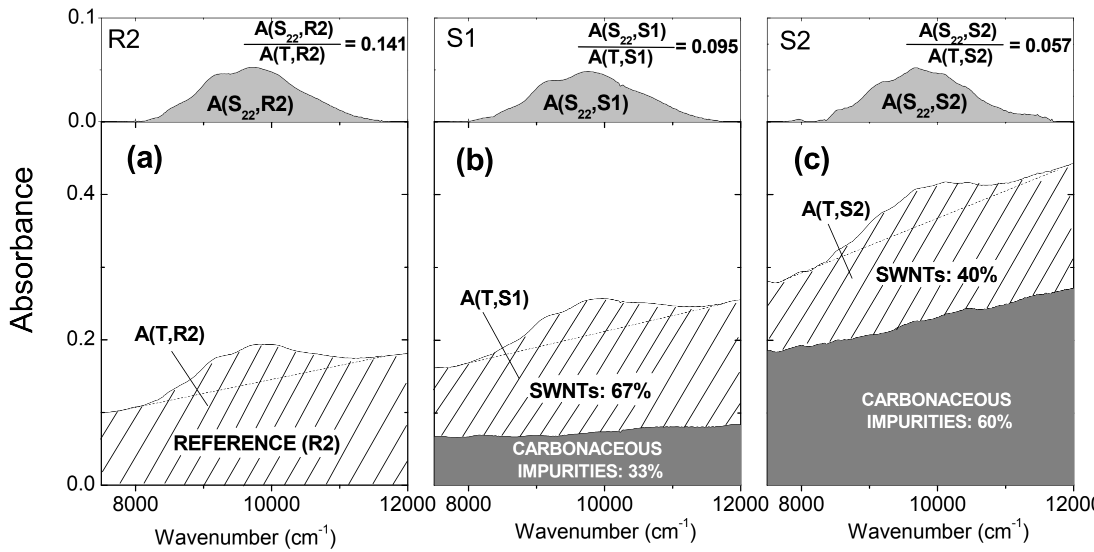
Future Work

Non-nanotube Carbon by NIR Absorption





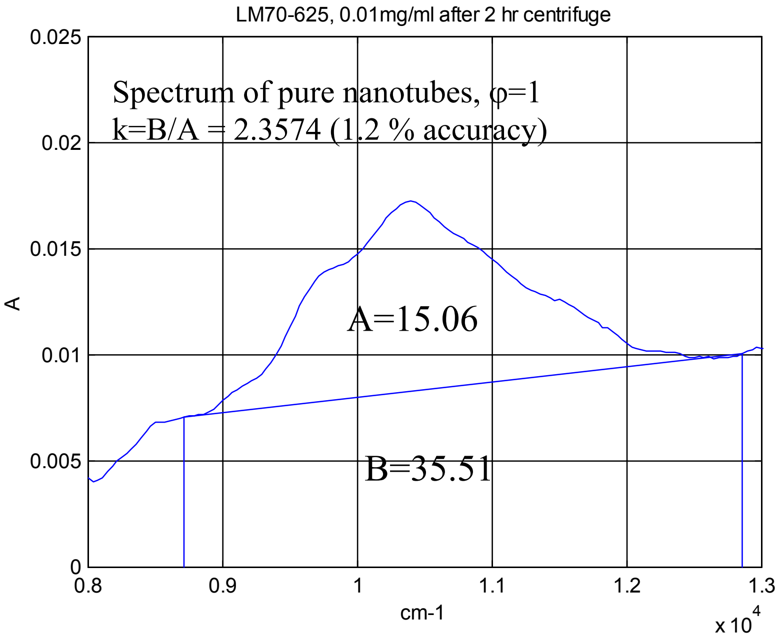




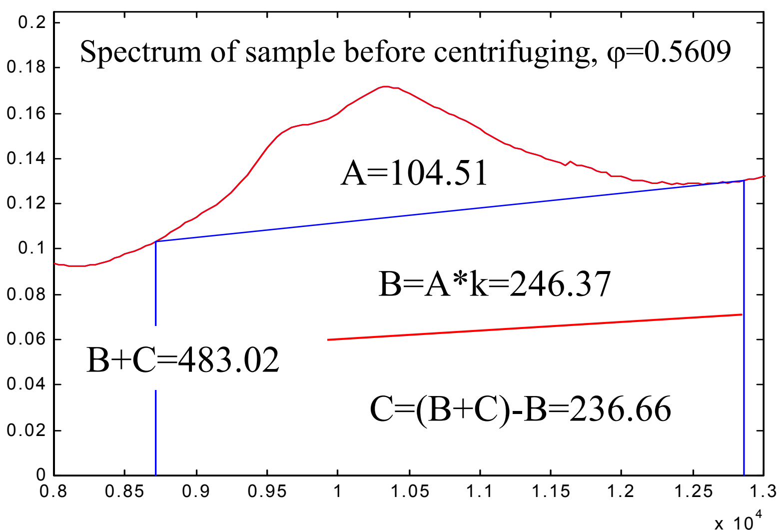
M. E. Itkis, et al. Nano Lett, **3**, 309 (2003)

Non-nanotube Carbon by NIR Absorption

JSC reference sample



LM70_20cm1.txt



A: NT Van-Hove absorption
B: NT plasmon absorption
C: Impurities plasmon absorption

Pure nanotubes: φ=1, **k = B/A = 2.3574**

Dirty nanotubes, φ=0.5609, B=*xφ*, C=*x(1-φ)ε*,

$$\varepsilon = \frac{\varphi}{1-\varphi}\frac{C}{B} = \mathbf{1.2270}$$, meaning that NT absorb 1.2270 times stronger in the plasmon region than carbonaceous impurities.

Non-nanotube Carbon by NIR Absorption

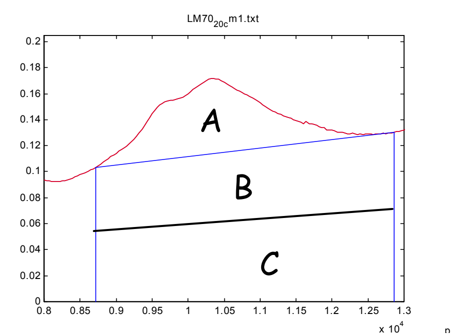
Now we have a nanotube purity standard – 100% laser SWCNT in DMF solution (~3.6 μg/ml)

k=B/A = 2.3574 (1.2 % accuracy), i.e. we can calculate NT plasmon absorption from NT Van Hove absorption.

ε=C/B=**1.2270** , i.e. absorption by NT is 1.2270 times stronger than absorption by carbonaceous impurities.

From this we can calculate absolute ratio of nanotubes to non-tubular carbon impurities in any laser NT sample, using the following strategy:

1. Measure A and (B+C)
2. Calculate B=kA
3. Calculate C=(B+C)-B
4. Calculate $\varphi = \dfrac{B}{B + C/\varepsilon}$



Combined with metal content measured by TGA, we know composition of the sample

How do We Perform Characterization?

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- **UV-Visible-Near Infrared (UV-Vis-NIR) Absorption**
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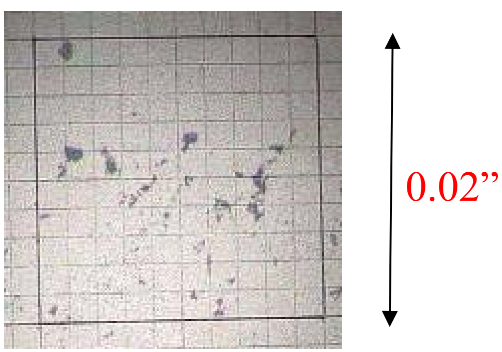
Purity and Dispersion

Macrodispersion and Nanodispersion

Optical Dispersion Analysis Protocol

Nikon V12A Comparator



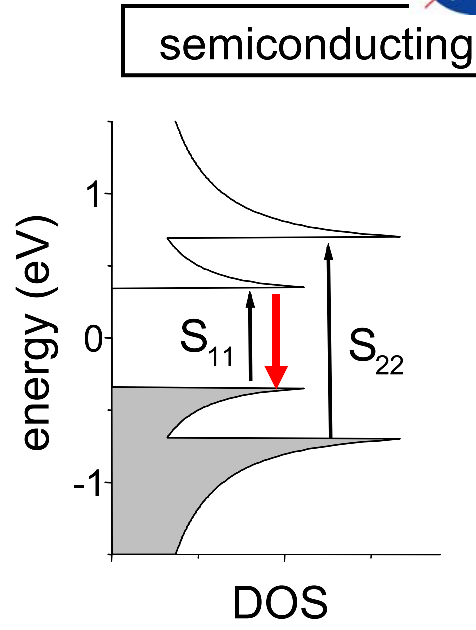
100X

Guidelines for a quantitative reproducible protocol:

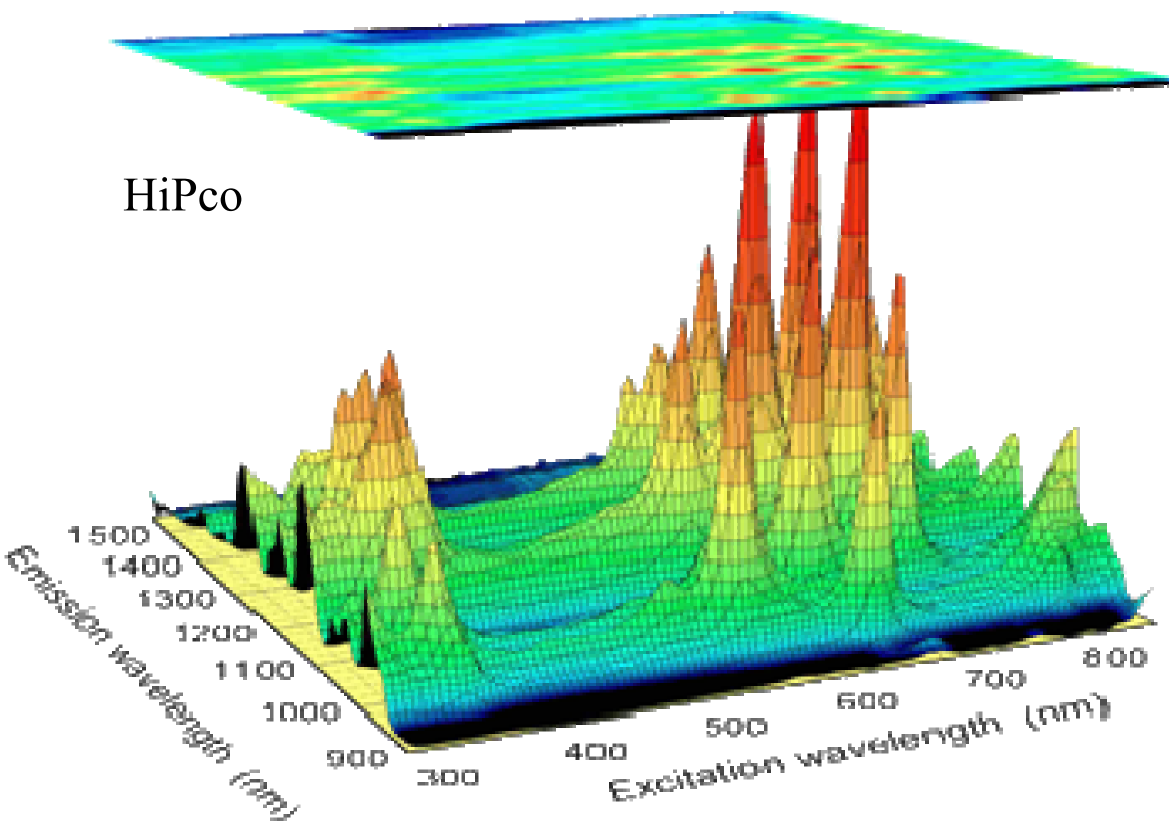
- Follow guidelines for UV-Vis protocol and establish dispersion grade (A, B, or C).
- Once dispersion grade has been assigned, sonicate sample (0.1 mg/ mL) for 1 hour.
- After 1 hour of sonication, allow sample to rest at room temperature for 1 hour.
- Stir sample thoroughly and remove an aliquot (17µL)
- *A volume of 17 µL 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

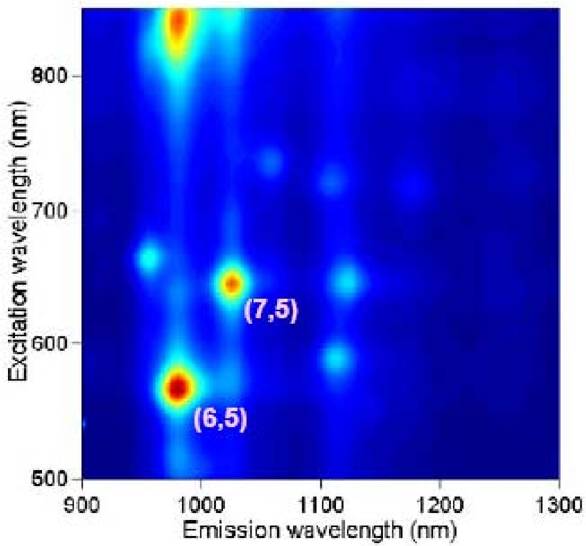
Chirality Determination



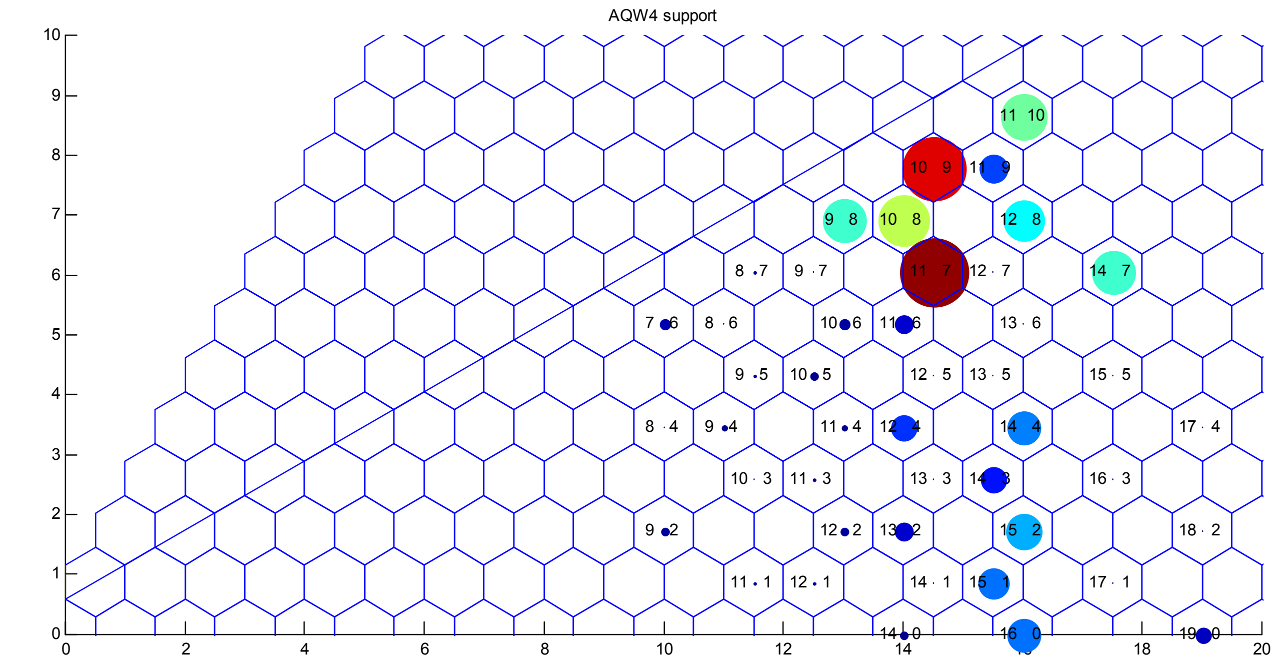
HiPco



Alcohol CVD



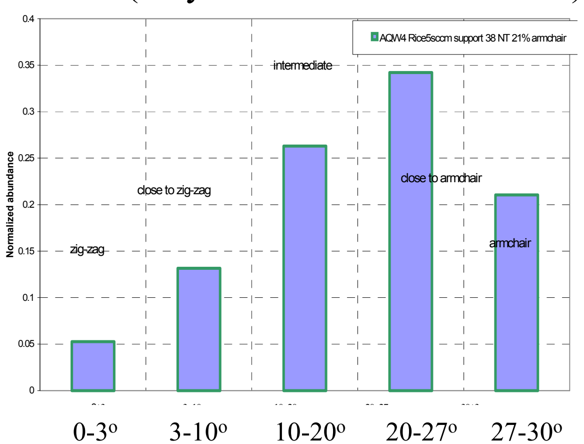
Fluorescence "map"



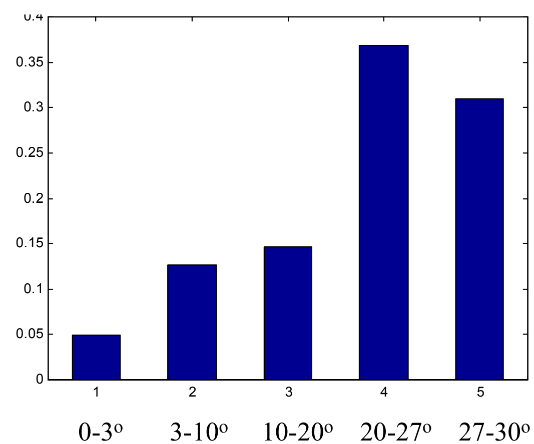
PLV nanotubes in D_2O / SDBS solution.

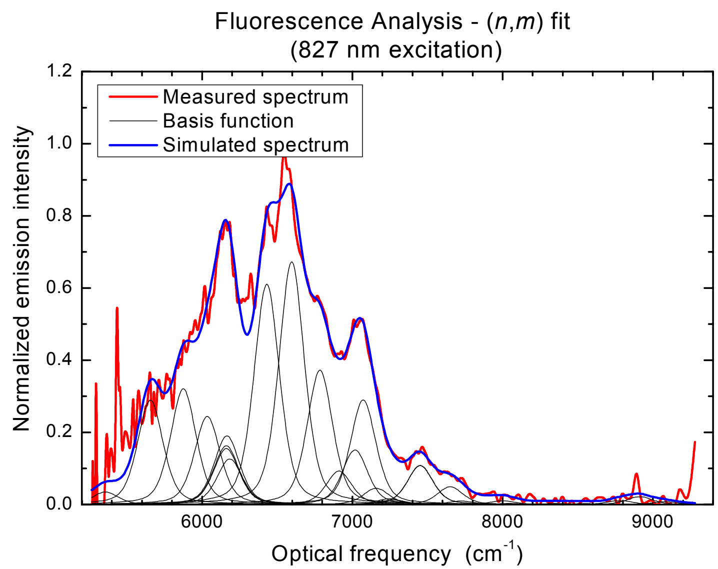
Chiral angle distributions:

From e-beam diffraction (very limited number of tubes)



From fluorescence (S_{11} only)





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

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NASA-NIST Collaboration

--Purity and Dispersion Workshops 2003, 2005 and upcoming in September 2007

--Practice Guides on web page

http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide.htm

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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Nanotube characterization standards

→ **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

Team Members

- Dr. Ram Allada
- Dr. Sivaram Arepalli
- Dr. Peter Boul
- Dr Kelley Bradley
- Dr. Olga Gorelik
- Mr. William Holmes
- Mr. Padraig Moloney
- Dr. George Nelson
- Dr. Pavel Nikolaev
- Dr. Maryjane O'Rourke
- Dr. Edward Sosa
- Mr. Mike Waid
- Dr. Leonard Yowell

JSC's Applied Nanotechnology Team, left to right: Pasha Nikolaev, Mary Jane O'Rourke, Ram Allada, Peter Boul, R. Kelley Bradley, Team Lead Leonard Yowell, Michael Waid, Chief Scientist Sivaram Arepalli, Padraig Moloney, William Holmes, George Nelson, Edward Sosa.

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

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