NASA-JSC protocol for the characterization of single-wall carbon nanotube material quality

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Abstract

It is well known that the raw as well as purified single wall carbon nanotube (SWCNT) material always contain certain amount of impurities of varying composition (mostly metal catalyst and non-tubular carbon). Particular purification method also creates defects and/or functional groups in the SWCNT material and therefore affects the its dispersability in solvents (important to subsequent application development). A number of analytical characterization tools have been used successfully in the past years to assess various properties of nanotube materials, but lack of standards makes it difficult to compare these measurements across the board. In this work we report the protocol developed at NASA-JSC which standardizes measurements using TEM, SEM, TGA, Raman and UV-Vis-NIR absorption techniques. Numerical measures are established for parameters such as metal content, homogeneity, thermal stability and dispersability, to allow easy comparison of SWCNT materials. We will also report on the recent progress in quantitative measurement of non-tubular carbon impurities and a possible purity standard for SWCNT materials.

Travel support provided by the organizers include plane ticket and Hotel.

NASA-JSC Protocol for the Characterization of Single Wall Carbon Nanotube Material Quality

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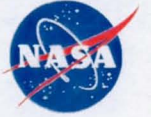[2] Texas Center for Superconductivity, University of Houston, Houston, TX

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Our goals:

- 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 take into account known inhomogeneity in nanotube specimens.

- 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)

JSC characterization protocol

TGA (thermogravimetric analysis)

- 3 runs on 3-4 mg of material

- Conditions: 100 sccm air, 5 °C/min heating rate, room temperature to 800°C

- Each run takes ~3 hrs. Apparently, baseline instability of TGA exceeds 10 μg over this time span. Therefore it is necessary to weigh the residue on the microbalance after each run and correct results accordingly.
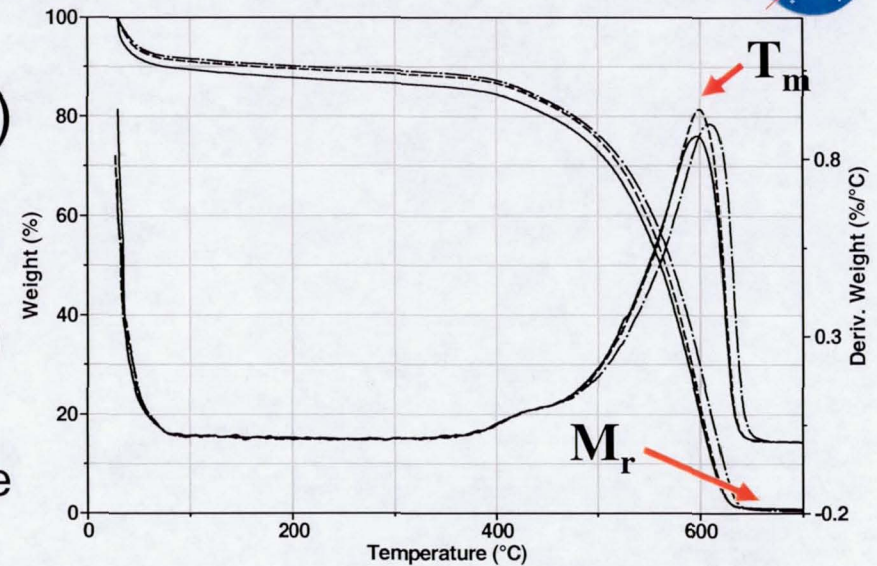
•Information extracted from TGA data:

1. Average residual mass M_r (in %): Shows **fraction of residual metals** in the specimen.

2. Temperature T_m of the maximum in the burning rate dm/dT : Shows **thermal stability** of the specimen.

3. Standard deviation of M_r and T_m: Shows **homogeneity** of the specimen

Example: TGA

Unpurified HiPco SWNT:

$M_r = 26.4 \pm 3.3 \%$; $T_m = 405.9 \pm 1.6\ ^{\circ}\text{C}$

Residual mass is large (consistent with unpurified HiPco nanotubes).

Homogeneity is better than in HP87R

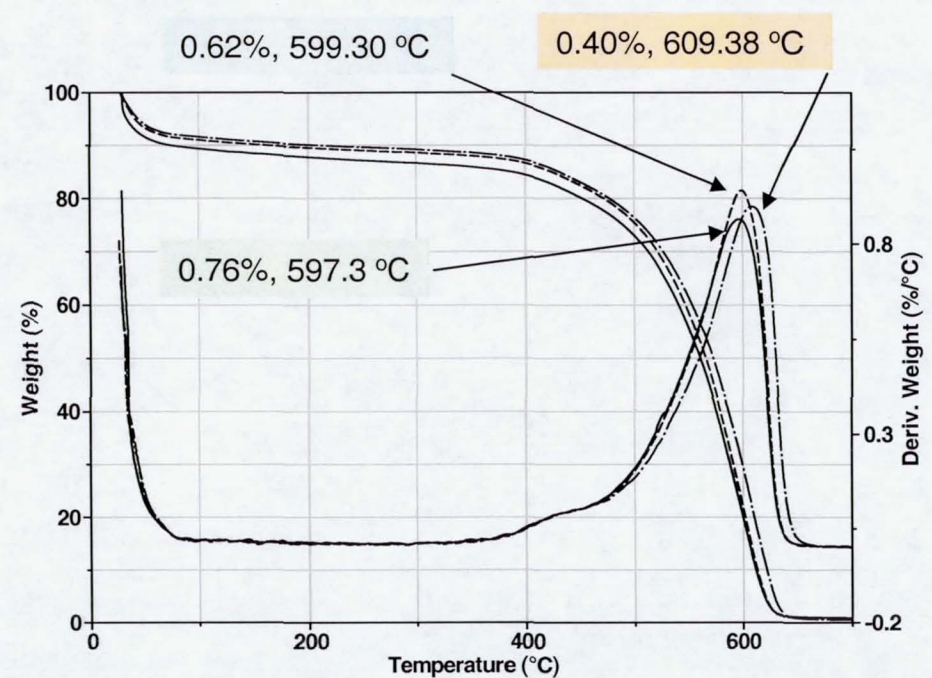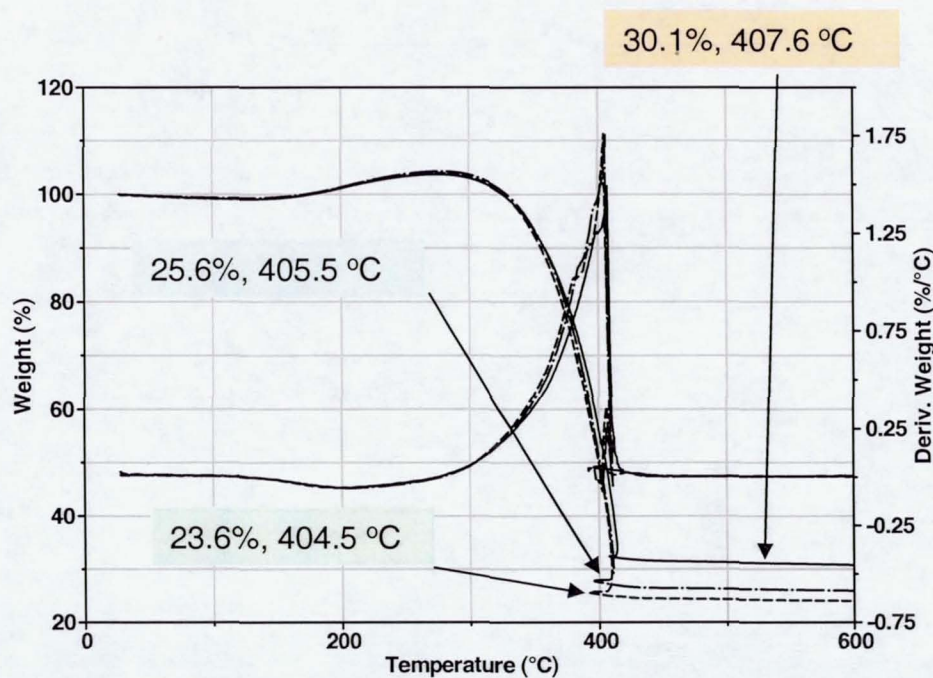Thermal stability is low (consistent with unpurified HiPco nanotubes)

Purified HiPco SWNT (HP87R):

$M_r = 0.59 \pm 0.18 \%$; $T_m = 602 \pm 6.5\ ^{\circ}\text{C}$

Residual mass is very small.

Homogeneity is good

Thermal stability is very high

JSC characterization protocol
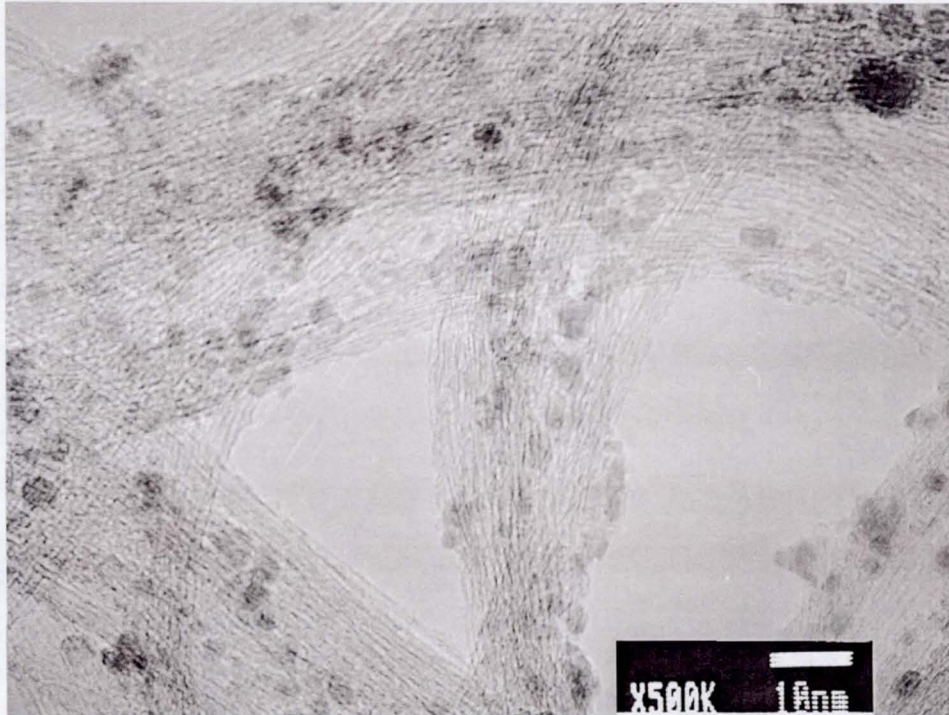
TEM (transmission electron microscopy)

- **Sample prep for TEM: A**bout 0.1 mg of material is bath sonicated in 20 ml of methanol for about 10 minutes. One drop of this suspension is placed on the TEM grid lying on a tissue paper. The grid is then dried in an oven at 120 °C for at least two hours.

- One specimen is imaged at 160 kV. There is usually more inhomogeneity within a single grid than between different grids, so it is deemed not necessary to image more than one specimen.

- Survey of relatively large area on the TEM grid, followed by taking 2 images at x500K, and one image at x200K (more images if necessary) of average-looking areas

- EDS of about 250x250 nm average-looking area at x40K, avoiding support film.

- **Information from TEM imaging and EDS:**

1. Images: Qualitative information about **non-nanotube carbon impurities** ("schmutz" and graphitic particles) and their distribution within a sample

2. Images: Qualitative information about **metal content**

3. EDS: Qualitative information about **metals, chlorine, oxygen, etc. impurities**
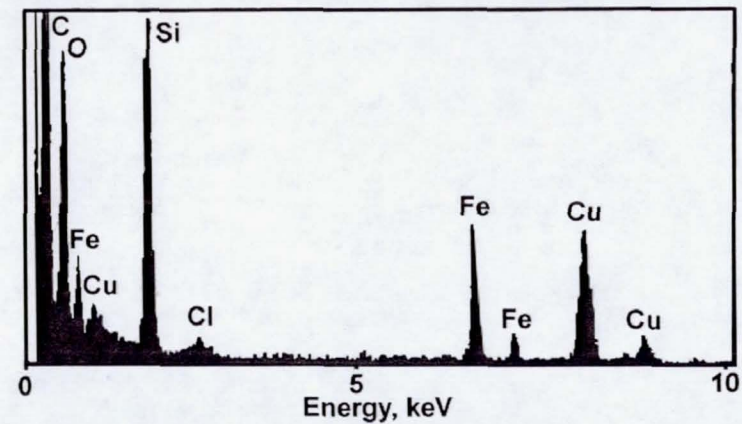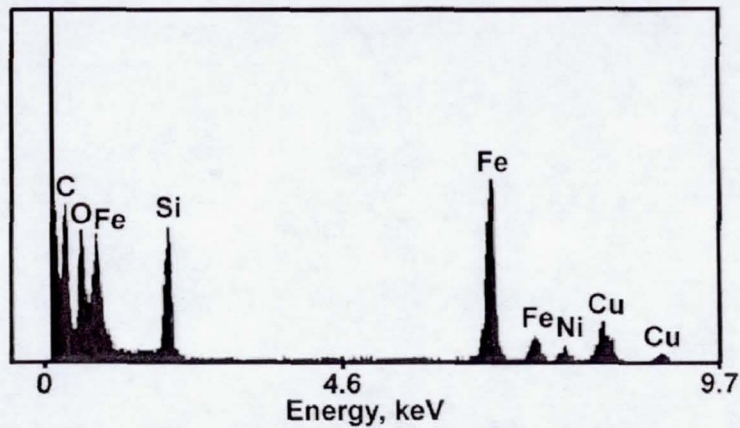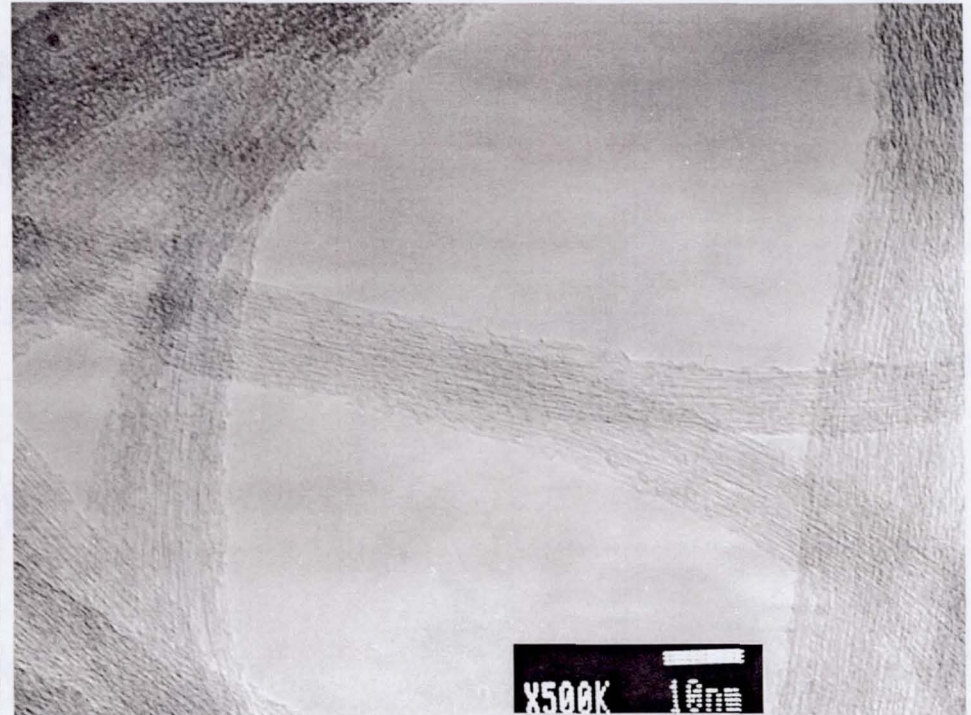
Example: TEM

Unpurified HiPco SWNT:

Some non-tubular carbon impurities, lots of Fe, some Oxygen and Si

Purified HiPco SWNT (HP87R):

Very little non-tubular carbon impurities, still some Fe, Oxygen and Si, some Cl (from purification)

JSC characterization protocol

SEM (transmission electron microscopy)

- **Sample prep for SEM:** Very small piece of material is mounted on SEM puck using double sided carbon tape. No platinum coating.

- One sample imaged at three different-looking places, 10kV, spot 3, WD 4mm, not coated. One image each at 20kX and 50kX magnification

- EDS spectrum collected at each of these points, 20kV, spot 3, WD 10mm, 2kX magnification, with Be window in. Spot size needs to be increased occasionally to increase the count rate. 20kV voltage is necessary to obtain a signal from metals. Be window is necessary to protect the detector from X-ray overload generated by lighter elements at 20kV.

- **Information from SEM and EDS:**

1. Images: Qualitative information about **impurities, general look of the sample and its homogeneity**

2. EDS: Qualitative information about about **metals, silicon and chlorine impurities**
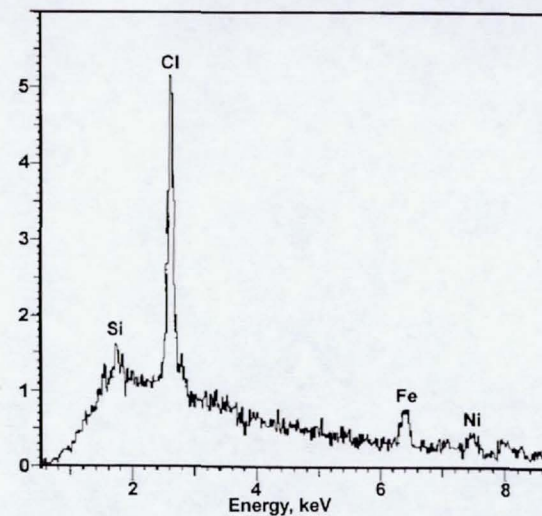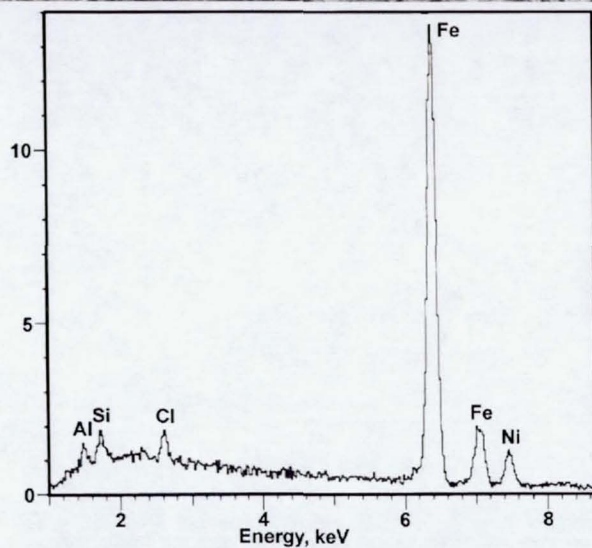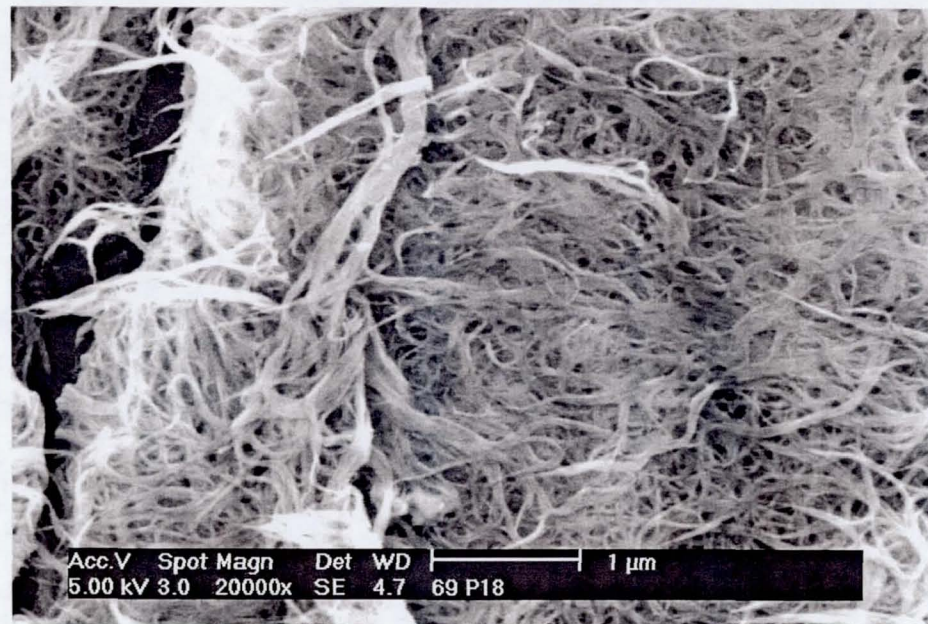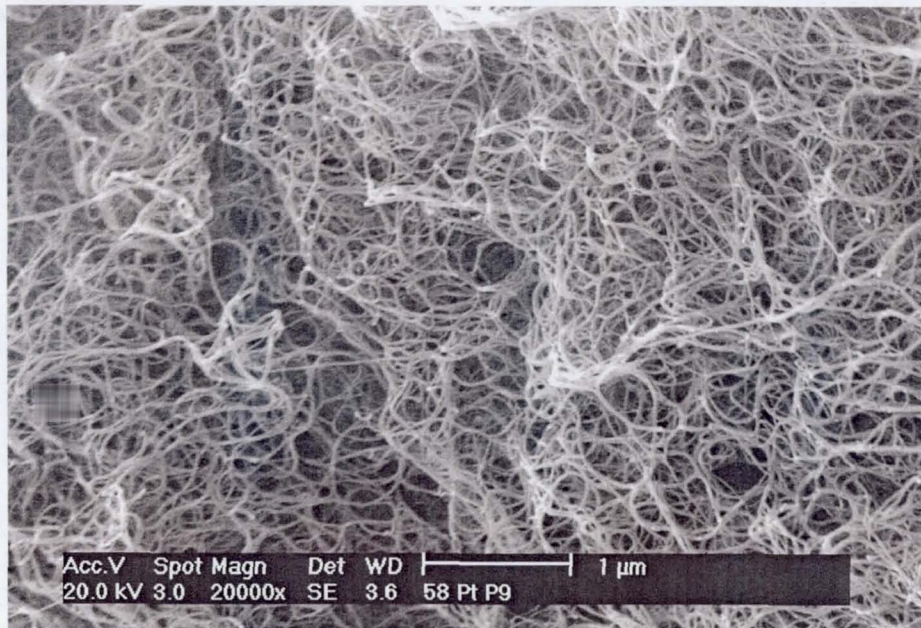
Example: SEM

Unpurified HiPco SWNT:

Uniformly abundant nanotubes, lots of Fe, some Cl and Si, Al (sample mount)

Purified HiPco SWNT (HP87R):

Uniformly abundant nanotubes, still some Fe, some Cl (from purification), Si (possibly glassware)

JSC characterization protocol

Raman spectroscopy

- Three continuous scans of three different places on a piece of nanotube material, 100-2000 cm^{-1} range, 15 sec. integration time, cosmic ray reduction on, 782 nm excitation laser wavelength.

- **Information from Raman spectra:**

1. Nanotube protonation state from the C-C stretch mode shift.

2. Possible information about impurities and disorder in the sample from the 1340 cm^{-1} disorder peak position and width

3. Qualitative information about sample homogeneity from the variability in the spectra

Example: Raman spectra

Unpurified HiPco SWNT:

Large variety of diameters (RB mode), weak D-band at 1295 cm^{-1}, only ~30 cm^{-1} wide (low disordered carbon), G-band at 1586 cm^{-1}, good uniformity of spectra taken at different places
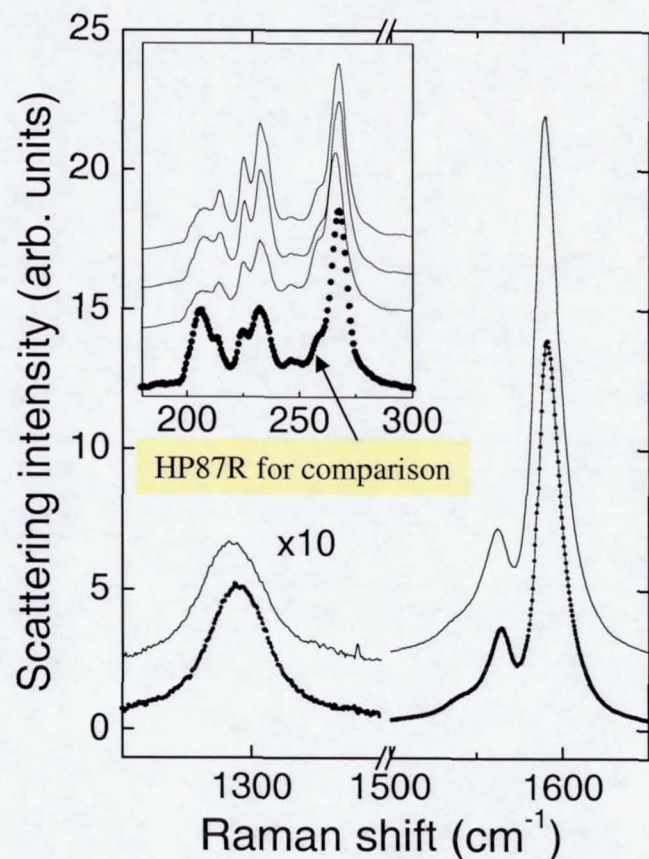
Purified HiPco SWNT (HP87R):

Purification slightly increases abundance of larger diameter nanotubes (RB mode), very similar D-band (low disordered carbon), G-band upshifted 1-2 cm^{-1} (weak protonation), good uniformity of spectra taken at different places
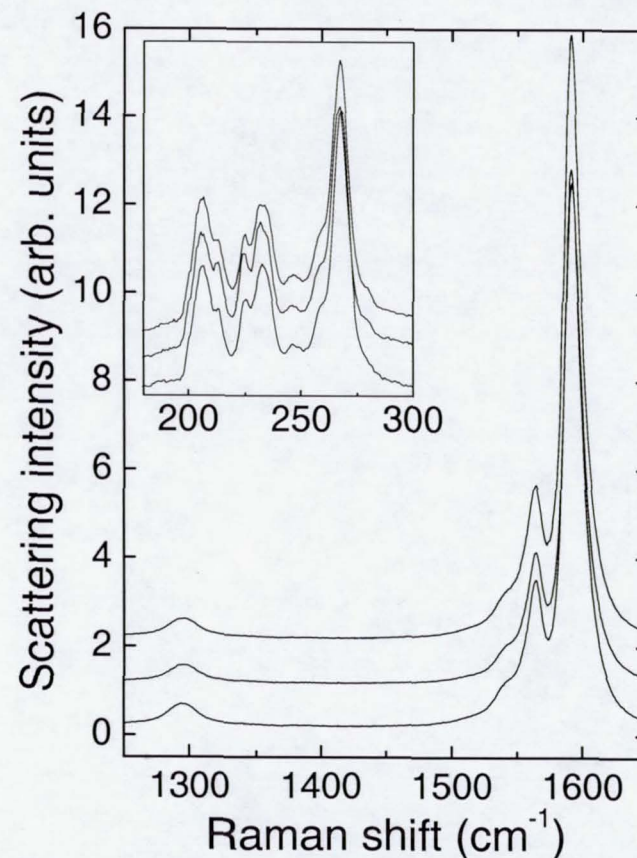
JSC characterization protocol

Sonication

•In composites work we often need to disperse nanotubes in organic solvent prior to introducing it into the polymer matrix. Therefore information about how well do nanotubes disperse and stay in suspension is of practical importance.

•Bath sonicate 3 separate samples, 0.1 mg each in 10 ml DMF (in 25 ml tall test tube). Sonicator conditions – 18 W, water level even with the level in test tube, centered in bath. Check every 15 minutes until one hour. If big chunks persist, then monitor at 4, 8, 24 hours, until these chunks disappear. Record this time and variability of these samples.

•**Information from sonication:**

- Provides quantitative information about **time required to disperse specimen by ultrasound.**

JSC characterization protocol
## UV-Visible spectroscopy

- Take one of these samples immediately from the sonication test for UV-VIS analysis. Use quartz cuvettes, record UV-VIS spectrum from 325 to 1400 nm. Repeat after one hour.

- Compare areas under the spectrum (from 700 to 1000 nm) and report percentage change. Also, record results of visual inspection of the suspension before and after the scans.

- **Information from UV-vis test:**

Provides quantitative information about **how well nanotubes stay in suspension**.
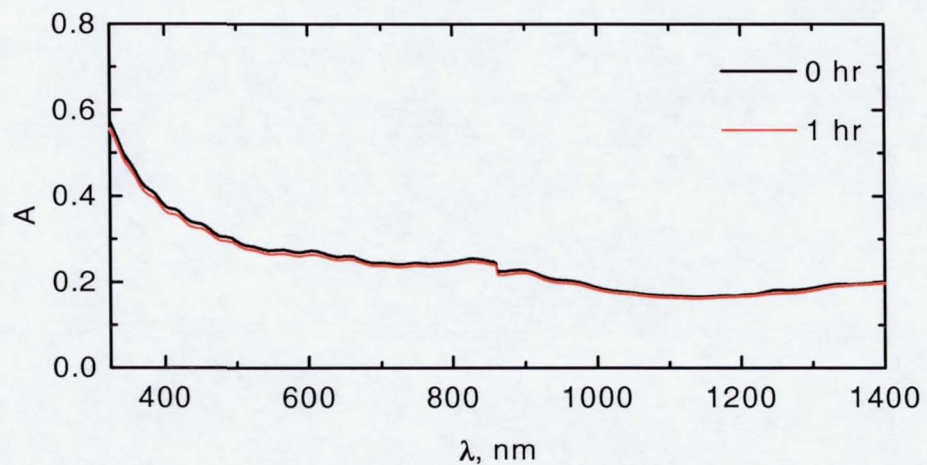
UV-Vis dispersability
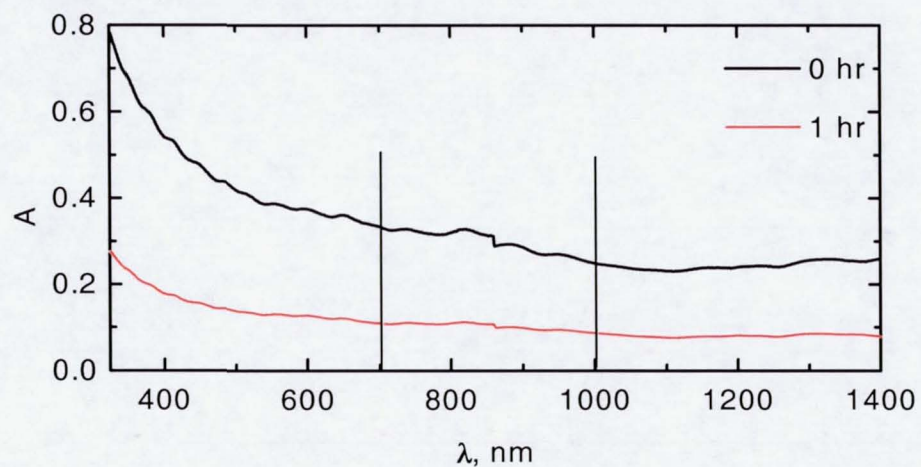
Unpurified HiPco SWNT:

Dispersed well in 30 min.

65.9% decrease in the area under the spectrum in 1 hour.

Purified HiPco SWNT (HP87R):

Dispersed well in 15 min.

2.95% decrease in the area under the spectrum in 1 hour.

Numerical measures of the properties of SWNT samples

Sample variables: residual mass (metal content), thermal stability, homogeneity, dispersability in DMF and stability in DMF suspension are now expressed in numerical form, which makes it easy to compare samples across the board.

Non-tubular carbon impurities are still assessed qualitatively from

TEM and SEM imaging ☹

	Unpurified	Purified
Metal content	$M_r = 26.4 \pm 3.3$ %;	$M_r = 0.59 \pm 0.18$ %;
Thermal stability (oxidation temperature)	$T_m = 405.9 \pm 1.6\ ^oC$	$T_m = 602 \pm 6.5\ ^oC$
Homogeneity	$\Delta M_r = 12.5\%,\ \Delta T_m = 0.4\%$	$\Delta M_r = 30.5\%,\ \Delta T_m = 1.1\%$
Ability to suspend (time to suspend in DMF)	30 min.	15 min.
Ability to stay in suspension (% change in absorption in 1 hour)	65.9%	2.95%

| Parameter	Technique	Analysis
Purity	TGA	Quantitative - residual mass after TGA in air at 5 °C/min to 800 °C. (metal content)
	SEM/TEM	Qualitative – amorphous carbon impurities
	EDS	Qualitative – metal content
	Raman	Qualitative – relative amount of carbon impurities and damage/disorder
Thermal Stability	TGA	Quantitative – burning temperature in TGA in air at 5 °C/min to 800 °C (dM/dT peak maximum)
Homogeneity	TGA	Quantitative – standard deviation of burning temperature and residual mass taken on 3 samples
	SEM/TEM	Qualitative – image comparison
Dispersability	Ultra-sonication	Quantitative – time required to fully disperse low concentration SWNT in DMF using standard settings/configuration
	UV-vis	Quantitative – relative change in absorption spectra of sonicated low conc. SWNT/DMF suspension

How do we obtain a reliable reference sample?

TPO (temperature programmed oxidation)

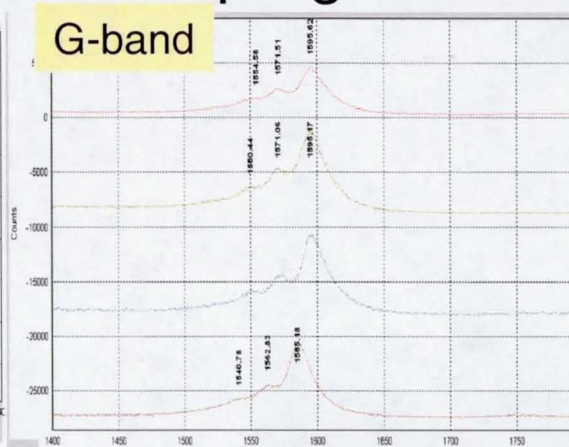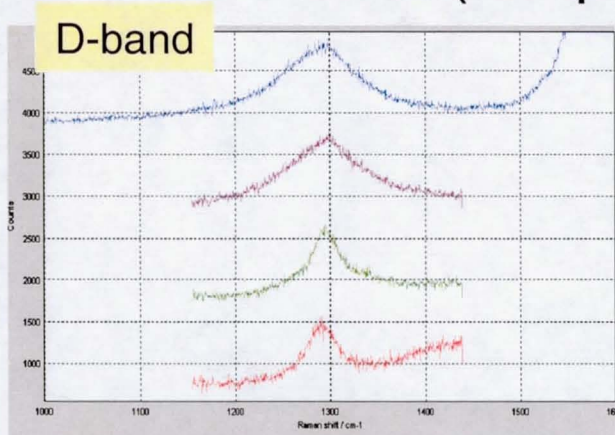Deconvolution of the weight loss profile: 5 peaks present.
Total area under peaks is 77.25%. With correction for 6% initial water loss and 17% residual mass total weight loss is ~100%, as expected. Note: the Gaussian fit of the first peak is probably unreliable.
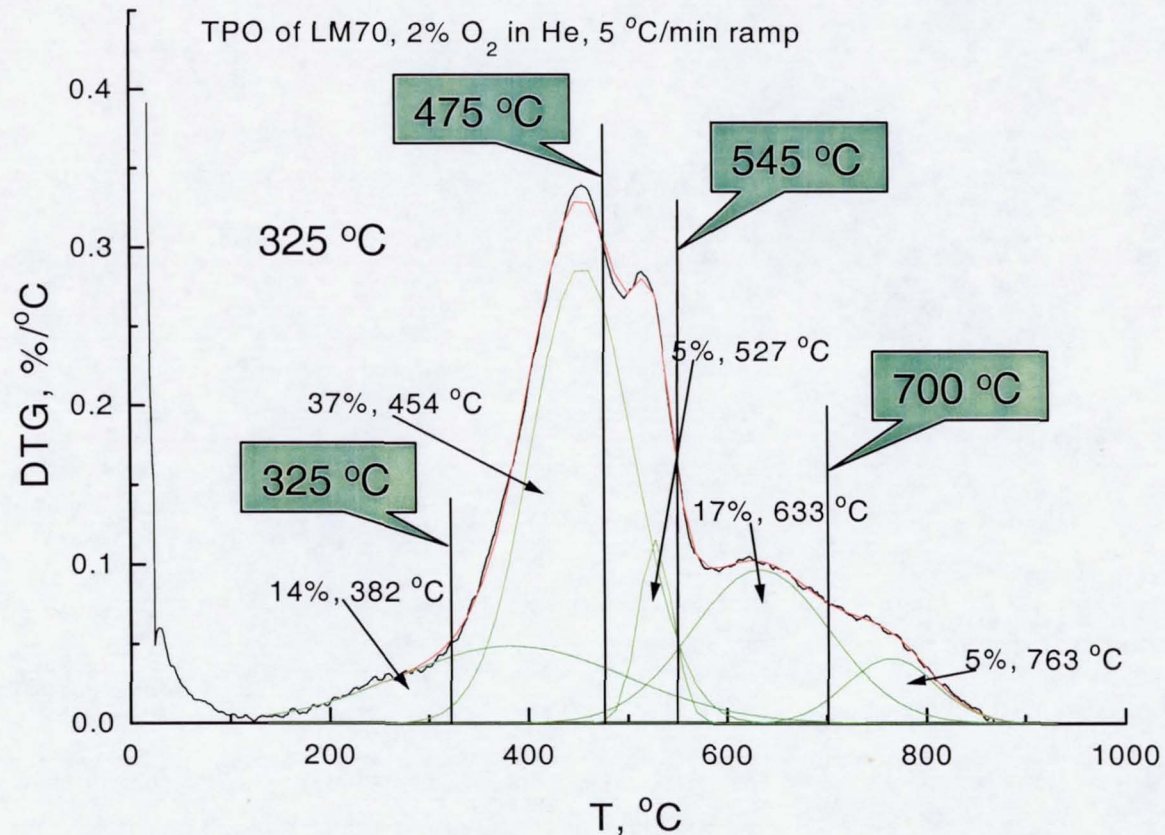
How do we obtain a reliable reference sample?

TPO (temperature programmed oxidation)

D-band

G-band

As-is: 1595 cm^{-1} G-band

325 °C: 1595 cm^{-1} G-band

475 °C: 1595 cm^{-1} G-band

545 °C: 1585 cm^{-1} G-band
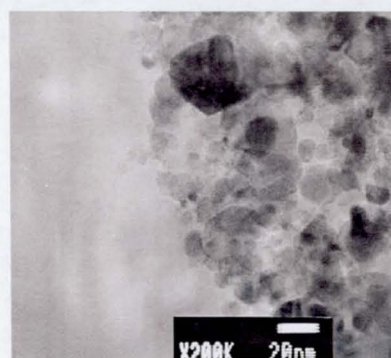
700 °C: no SWNT signal

325 °C: similar to as-is

475 °C: similar to as-is but less non-tubular impurities

545 °C: even less non-tubular impurities, metal particles starting to lose graphitic coating

700 °C: no SWNT found, metal particles mostly free of graphitic coating