

Raman Spectroscopic Assessment of Purification Methods for Single Walled Carbon

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Key Words

As Produced (AP), Laminar Flow Deposition (LFD) Purification, Ring Breathing Modes (RBM), Single Walled Carbon Nanotubes (SWCNT)

Single Walled Carbon Nanotubes (SWCNT's) hold tremendous promise in a variety of areas due to their unique physical and electronic properties. These properties include high electronic mobilities, high tensile strength, high transparency, and high heat conductivity. These materials are being investigated for use in a number of key application areas that include but are not limited to: microelectronics, photovoltaics, and sensors. Synthetic routes involving arc discharge methods have made SWCNT's more accessible to researchers over the last few years. However, As Produced (AP) SWCNT can vary significantly in regards to quality from batch to batch and from vendor to vendor. AP SWCNT's may contain residual catalysts which may be in the form of metal nanoparticles, there may be MWCNT present and likely there will also be amorphous carbon and damaged SWCNT's. All of the above species are considered to be impurities which will have a deleterious effect on the observed properties of a device if the AP SWCNT's were used without further purification. This application note describes the results of two approaches to purify and enrich a bulk collection of AP SWCNT's highlighting how Raman, specifically the Thermo Scientific™ DXR Raman microscope can be used to gauge the effectiveness of purification and enrichment methods.



Purification of AP SWCNT Using Surfactant Encapsulation

The first method was reported by Bhatt, Vichchulada, and Lay of the University of Georgia¹. Their approach involved a three step process in which the bulk collection of SWCNT's were 1) encapsulated in a surfactant to form a suspension 2) subjecting this suspension to low centripetal force centrifugation and 3) using laminar flow deposition (LFD) on the different centrifugation fractions obtained from step two. This approach avoided more common approaches of using oxidizing reagents to help solubilize the carbon nanotubes. The oxidizing agents modify the surface of the SWCNT through additional hydroxyl groups, thus compromising the chemical properties.

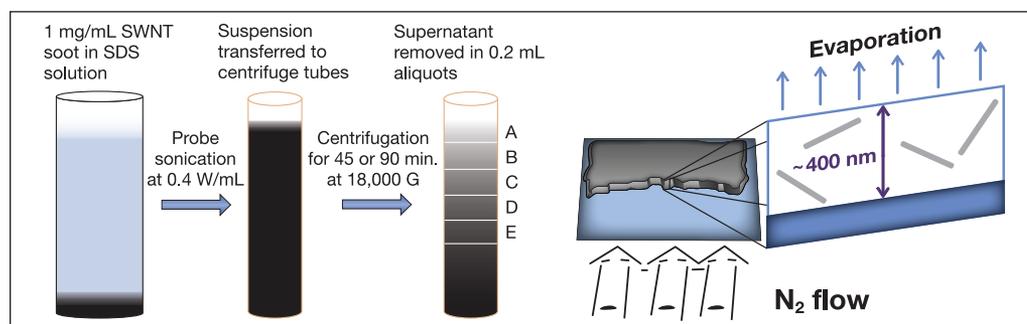


Figure 1: Three step separation process employed by Bhatt and Coworkers

How was Raman Used in this Study

Raman spectroscopy is well suited for assessing the extent of purification this method achieves. There are two spectral features present in the Raman spectrum of SWCNT's that can be used for this purpose. These are designated as the D and G bands that occur ~ 1340 and ~ 1590 cm^{-1} , respectively. (See Figure 2.) The D band (aka the disorder or defect band) is the asymmetric stretch indicative of sp^2 hybridized amorphous carbon and/or indicative of the presence of defects in the wall of the SWCNT. The G band (aka the Graphitic band), is the symmetric tangential mode associated with pristine SWCNT's. Thus, for highly pure SWCNT it is expected that the spectrum should have a very high intensity for the G band and little or no D band. Bhatt and coworkers recognized that they could use the ratio of the intensity of the G to D (I_G/I_D) bands as a benchmark to assess the elimination of impurities (amorphous carbon and damaged nanotubes).

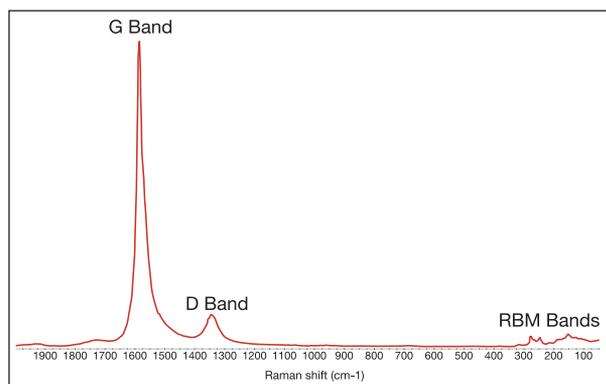


Figure 2: The Raman spectrum of AP SWCNT showing the D and G band. Also indicated on the spectrum are the ring breathing modes (RBM) that occur at low frequency. The peak positions of these modes correspond to different diameter SWCNT.

Care must be taken into account when measuring the Raman spectrum of carbon nanotubes, especially when collecting the Raman spectrum from a deposited or solid sample. It is absolutely necessary to precisely control the laser power being directed to the sample during measurement since operating at high laser powers can induce spectral shifts and/or damage to the collection of tubes (increasing the intensity of the D band). It is also necessary that the power level chosen is reproducibly applied for all measurements. The DXR Microscope is particularly well suited to meet the stringent needs of precise and reproducible laser power control at sample. The DXR microscope has a patented* laser power control feature that allows the analyst to set up an experimental method that defines precisely the laser power delivered to the sample in mW (not in % of laser full power as other commercial instruments do) from 0 to maximum power of the laser at 0.1 mW increments. This allows the analysts to reliably and accurately set the power for every measurement. Additionally, the DXR has the only on demand auto alignment/calibration tool that 1) precisely aligns the three principle light paths of the instrument relative to each other and 2) provides full calibration of the instrument (wavelength,

laser frequency, and Raman intensity) which is achieved through multipoint calibrations across calibrations using three built-in standards. This alignment/calibration is fast and easy to perform, taking just a few minutes. The on demand automated alignment ensures the instrument is in its highest performing condition giving the highest possible sensitivity. This allows measurements to be performed at lower laser powers on samples like SWCNT which are sensitive to photo damage.

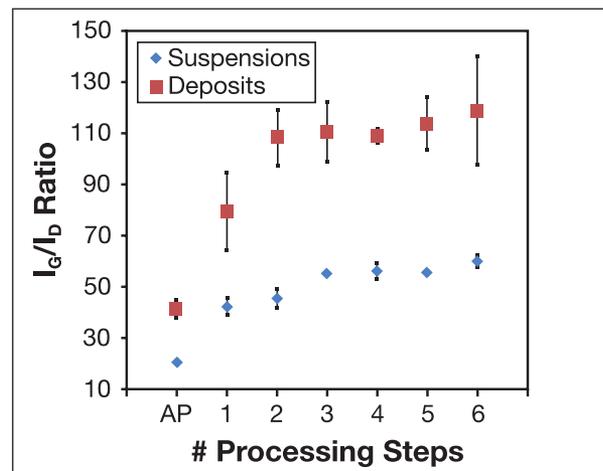


Figure 3: Plot of G to D band through six cycles of Purification. It is apparent that the Laminar Deposition Step is playing a key role in enhancing the purification.¹

Bhatt and his coworkers used the DXR Microscope to measure the I_G/I_D band ratio for both suspension and deposited SWCNT's. The results show several measurements covering suspension and LFD depositions of AP SWCNT's through six cycles of surfactant encapsulation, low centripetal ultracentrifugation, and LFD. (Figure 3) It can be clearly seen from the figure that the ratio increases almost 300% after two processing steps proving that this method is an effective means of purifying the AP SWCNT's.

Purification and Separation of AP SWCNT's – Isolation of Semiconducting SWCNT's

Another application which is very well suited for Raman spectroscopy is in the separation of SWCNT exhibiting either purely semiconduction or metallic properties. Shea and Arnold⁴ at the University of Wisconsin undertook the evaluation/separation of AP SWCNT. Understanding that during SWCNT synthesis both semiconducting and metallic single-walled carbon nanotubes exist in a 2:1 ratio, respectively, it is necessary to separate the two species from each other. Semiconducting single-walled carbon nanotubes (s-SWCNTs) are desirable for technological applications including transistors, light-emitting diodes, and photo detectors. The presence of even small quantities of metallic or multi-walled nanotubes severely degrades device performance. Therefore, separation of single-walled from multi-walled, and semiconducting from metallic nanotubes is vital to achieving high-quality technologically relevant devices incorporating s-SWCNTs.

* US patent number 6,661,509 B2

Previously, the polymer poly (9,9-dioctylfluorene) (PFO) has been shown to selectively wrap s-SWCNTs, which solubilizes these specific nanotubes and allows them to be separated from multi-walled nanotubes, metallic single walled nanotubes, and reaction catalyst.² The absorption spectrum of the resulting solution may be used to obtain the chirality distribution in the extracted solution. Raman characterization of separated s-SWCNT potentially offers an alternative method for determining separation efficacy.

How was Raman Used

Films of nanotubes were prepared by drop casting from solutions of raw CNT powder (Southwest NanoTechnologies) (1 mg/mL) and PFO (American Dye Source, Inc.) (2 mg/mL) in toluene, and from a solution of PFO-separated s-SWCNT (<0.01 mg/mL) and PFO (2 mg/mL) in toluene onto quartz slides. Figure 4 shows the low RBM region Raman spectra of the raw mixture of carbon nanotubes and the separated s-SWCNT collected on the DXR Microscope. Each peak in the Raman spectrum represents a distinct diameter of carbon nanotubes. There are large differences between spectra of the raw and PFO-separated carbon nanotubes. From these spectra, it is evident that during the separation process specific chiralities of carbon nanotubes are isolated from the raw mixture, which is an expected result of the PFO separation procedure.

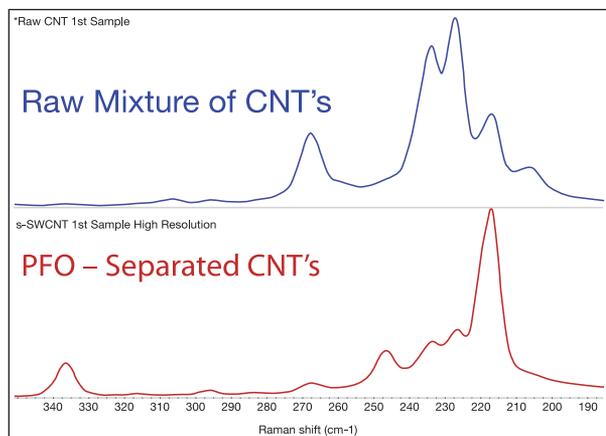


Figure 4: RBM region Raman spectrum of AP SWCNT (top, blue) spectrum, purified SWCNT (bottom, red) spectrum. Peak position difference between the two spectra are consistent with a change in the distribution of the semiconductor vs. metallic SWCNT's. Note, there was also a decrease in the absorbance at 242 nm (not shown) which are indicative of elimination of amorphous carbon impurities by this same process.

Summary

In summary, Raman spectroscopy provides useful information when characterizing a collection of carbon nanotubes when applied with care. It was shown how Raman spectroscopy was used to determine the efficacy of two different purification/separation techniques. In particular it was demonstrated how the Thermo Scientific DXR Raman microscope with its on demand automated alignment and calibration features and exquisite laser power control is particularly well suited for this important application.

References

1. Bhatt, N. P., Vichchulada, P., Lay, M.D. Bulk Purification and Deposition Methods for Selective Enrichment in High Aspect Ratio Single Walled Carbon Nanotubes. *J. Amer. Chemical Soc.* **134**, 9352-9361 (2012)
2. Dresselhaus, M. A., Dresselhaus, G., Saito, R., & Jorio, A. Raman spectroscopy of carbon nanotubes. *Physics Reports* **409**, 47-99 (2004).
3. Nish, A., Hwang, J., Doig, J., Nicholas, R. Highly selective dispersion of single-walled carbon nanotubes using aromatic polymers. *Nature Nanotechnology* **2**, 640-646 (2007)
4. Matthew Shea and Michael Arnold, unpublished work, University of Wisconsin.

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