WHITEPAPER

The Characterization of Single Wall Carbon Nanotubes Using The Malvern Instruments' Helix System: Integrating Dynamic Light Scattering (DLS) and Raman Spectroscopy

Executive Summary

The combination of DLS and Raman spectroscopy offers the ability to measure the length, diameter, and chirality of carbon nanotubes in a single experiment. These parameters can be used with existing empirical knowledge of nanotubes to predict their conductivity and strength characteristics.

Dynamic Light Scattering (DLS) is widely accepted as a method for determining the hydrodynamic radius of nanoscale particles in suspension. While the use of DLS to determine the size of non-spherical particles (such as nanotubes) presents unique challenges, analytical methods have been developed to extract this information from the data.

Raman spectroscopy collects detailed structural information through access to fundamental molecular vibrations. The positions, shapes and intensities of the resulting bands can provide insight into structural details of the species under investigation. A wealth of publications document the use of Raman spectroscopy to characterize carbon nanotubes, including chirality and quality parameters.

Introduction

Owing to their readily-tunable thermal and electrical properties, incredible strength, and novel optical properties, carbon nanotubes (CNTs) have quickly established their place in existing commercial products where currently 75% of CNT applications are being developed in the energy, electronics and composites sectors.[1] Moreover, they offer immense promise for future medical and consumer product development. Estimates conclude that government nanotechnology funding will eclipse $1.0 billion per year in at least five countries by 2014,[2] totaling more than $12 billion worldwide. In 2011, the revenue for CNT work was approximated to be $300 million and by 2016, production volume is expected to see a 50% increase from today's levels.[1]

CNTs are primarily produced in the form of multi-wall nanotubes (MWNTs), comprising multiple layers of cylinders of graphene, because of their cost-effectiveness relative to their single-wall counterpart (SWNTs). However for specific applications, where a well-characterized, defect-free system is preferred, the unique electronic and mechanical properties that SWNTs offer are desired. Because of the continuing trend toward the miniaturization of electronics, demand for SWNTs should increase which will encourage more cost-effective production and purification methods.[3]

The proliferation of carbon nanotubes in research and commercial applications has led to the need for unique analytical approaches that can rapidly characterize them. Determination of the structure of the nanotubes, defined by their chiral index (x, y),[4] is critical to understanding their conductive properties. Likewise, the length and diameter of the structures are important to predicting their behavior during commercial applications. As no single technique is capable of providing all of the required information, a hybrid technique is a natural approach to elucidating the needed parameters. The combination of Dynamic Light Scattering (DLS) and Raman spectroscopy offers the potential to provide the structural information needed to characterize these samples.

The frequency of the radial breathing mode (v_{RBM}) measured by Raman spectroscopy has been used as a direct probe of the chirality, and therefore diameter, of single-walled carbon nanotubes (SWNT).[5] The position of the RBM band is sensitive to changes in the bonding structure of the nanotube, and its chirality. Thus, both the chirality and the diameter of the SWNT's can be determined by Raman spectroscopy.

DLS has seen widespread use as a technique for characterizing the hydrodynamic radius of nanoscale materials in suspension. Brownian motion of particles results in fluctuations of the intensity of scattered light, the time scale of which is related to the particle size. Although DLS assumes a spherical particle, corrections can be made to compensate for the high aspect ratio of nanotubes. An effective length can thereby be extracted from the results, which when coupled with an analysis of the RBM band, allows the accurate determination of nanotube length.

Materials and Methods

A Helix[6] from Malvern Instruments has been used to obtain DLS (nanoscale particle size) and Raman (structural information) data sequentially on a single sample. The Helix system uses a proprietary non-invasive backscatter (NIBS) detector with dynamic (DLS), static (SLS) and electrophoretic (ELS) light scattering to measure the hydrodynamic radius of particles from 0.15 nm to 5 µm. Raman spectra are collected using 785 nm excitation (~280 mW) from 150 to 1925 cm^{-1} at 4 cm^{-1} resolution.

SWNT samples containing a mixture of chiralities were prepared by tip-sonicating 2 mg of SWNT powder in a 10 mL solution of 0.2% w/w chitosan and 1% w/v acetic acid in Nanopure DI water to produce a stable dispersion consisting of individual nanotubes complexed with chitosan. Sample aliquots (~50 µL) are placed into a proprietary cuvette with thin quartz windows and positioned in a temperature controlled compartment (4 to 90°C ± 0.1°C). The data described here were collected at 25°C.

Results and Discussion

Raman spectroscopy can reveal a wealth of information about a nanotube sample. A characteristic spectrum of nanotubes consists of the radial breathing mode (100 - 350 cm^{-1}), D mode (~1300 cm^{-1}) and G mode (~1600 cm^{-1}). The D mode is an indicator of structural defects which can be caused by the presence of $C(sp^3)$-$C(sp^3)$ bonds while the G mode corresponds to the vibrations of the $C(sp^2)$-$C(sp^2)$ bonds composing the tube. The quality factor of nanotubes can be measured using the following equation (eqn 1):[7]

$$Q = 1 - \frac{D - B}{G - B} \qquad (\mathbf{1})$$

D represents the maximum intensity peak of the D-band, G represents the peak of the G-band and B represents the minimum value between the peaks associated with D- and G-bands (Figure 1). Q ranges from 0 to 1 where 1 is indicative of perfect quality. It is good practice to measure Q for each batch because a significant number of defects will detrimentally affect the mechanical and electrical properties of SWNTs.[8]

To demonstrate Raman spectroscopy's ability to evaluate quality, a commercial batch of SWNTs containing several chiralities was centrifuged at 21000 x g after suspending in a solution of chitosan. Since defective nanotubes tend to be more prone to aggregation, they will sediment during centrifugation.[9] With Raman spectroscopy, Figure 1 illustrates that the change in quality of a SWNT sample can be monitored.

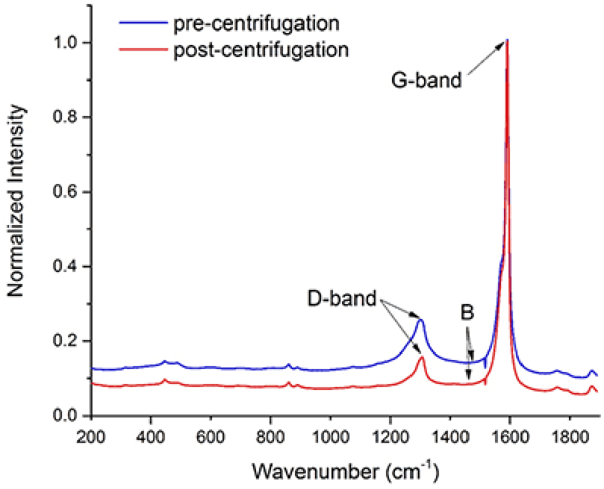

Figure 1: Raman spectra of a batch of carbon nanotubes before (blue) and after purification (red) via centrifugation. The intensity of the two spectra was normalized with respect to the maximum height of their G-bands.

According to eqn. 1, the Q factor for the commercially available batch (pre-centrifugation) is 0.87 while the Q factor after centrifugation is 0.92. This increase in the Q factor suggests that after centrifugation, some of the defective nanotubes can be removed and most importantly, the data indicates that Raman spectroscopy can be used to evaluate the quality of a batch of SWNT.

The radial breathing mode (RBM) region of a Raman spectrum can show the chiralities and, in turn, the diameters of the various species that are present in a nanotube mixture. The diameter of a SWNT (d) can be expressed in nanometers as a function of the RBM frequency (v) in cm^{-1} by the following (eqn. 2):[5]

$$d = \frac{214}{\nu - 19} \qquad (\mathbf{2})$$

The diameter of the SWNT can also be expressed as a function of the chirality indices (x, y) in eqn. 3:[5]

$$d = \frac{0.2462}{\pi}(x^2 + xy + y^2)^{1/2} \qquad (\mathbf{3})$$

Combining eqns 2 and 3 yields eqn. 4 that directly relates the RBM frequency from the Raman spectrum to the chirality of the SWNT.

$$\nu = \frac{869\pi}{(x^2 + xy + y^2)^{1/2}} + 19 \qquad (\mathbf{4})$$

From these equations, the relative purity of a specific batch of SWNTs can be evaluated by identifying the desired peak in relation to any neighboring ones. The frequency of the desired peak is determined through eqn. 4 by inputting the known indices of the SWNT. For example, the Raman spectra of two commercial batches of (6,5) and (7,6) show the presence of other chiralities in the RBM region (Figure 2).

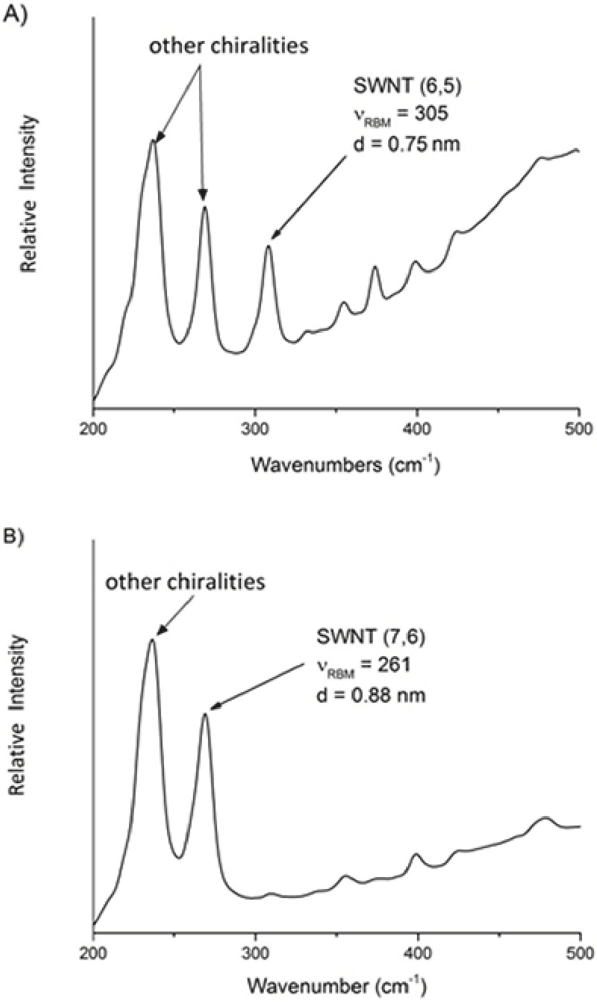

Figure 2: Raman spectra of two commercial samples advertised as primarily A) 6,5 and B) 7,6. From these mixtures, the relative purity of a desired chirality can be ascertained.

Data collected from dynamic light scattering (DLS) yields the size distribution as a bulk average of particles diffusing in solution. It assumes a spherical particle with an aspect ratio of 1. However, due to its cylindrical nature, a nanotube has an aspect ratio of about 1000, but its hydrodynamic diameter can still be accurately determined by DLS and verified theoretically with the following eqns (5 and 6)[10] describing the diffusion coefficients:

$$\mathrm{D} = \frac{\mathrm{kT}}{3\pi\eta\mathrm{L}}\left[\ln\left(\frac{\mathrm{L}}{\mathrm{d}}\right) + 0.32\right] \quad (\mathbf{5})$$

$$\mathrm{D} = \frac{\mathrm{kT}}{3\pi\eta\mathrm{D_h}} \quad \text{Stokes} - \text{Einstein} \quad (\mathbf{6})$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is temperature, η is the viscosity, D_h is the hydrodynamic diameter, and L and d are the length and diameter of the nanotube, respectively. Combining the equations relates D_h to the dimensions of the nanotube in the form of eqn 7:

$$D_h = \frac{L}{\ln\left(\frac{L}{d}\right) + 0.32} \quad (\mathbf{7})$$

The Helix which couples DLS measurements and Raman spectroscopy conveniently allows the acquisition of diameter and length data from a single batch of SWNTs. Using eqn 6, the theoretical hydrodynamic diameter of (6,5) nanotubes with a radial diameter of 0.75 nm as determined from Raman spectroscopy, and a length of at least 700 nm,[11] is 100 nm. This theoretical hydrodynamic diameter is in excellent agreement with the hydrodynamic diameter (91 - 106 nm) obtained through the integrated DLS measurement (Figure 3). Moreover if the length of the nanotube were unknown, it can be calculated with the same equation using the measured hydrodynamic diameter from the DLS (assume 100 nm based on the DLS range) and the diameter from the Raman (0.75 nm) to obtain about 720 nm, which is in agreement with the value (> 700 nm) from Sigma-Aldrich.[11] Given the high aspect ratio (1000:1) that is inherent in the SWNT, it is important to note that the smallest inaccuracy in the DLS measurement of the hydrodynamic diameter would result in dramatic changes in the calculated length. Therefore the calculated length should be considered as only an approximation.

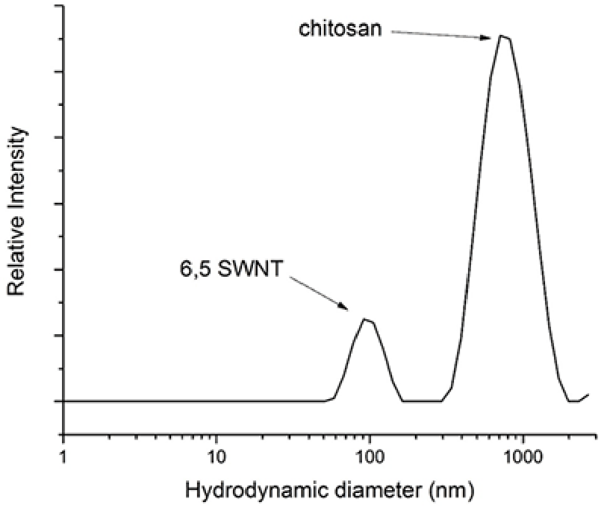

Figure 3: Graph depicting a DLS measurement of a suspension of (6,5)-SWNT dispersed in 0.2% w/w chitosan in water. The DLS measurement was graphed as an average of 14 runs and chitosan has a molecular weight ranging from 190 - 310 kDa.

Conclusion

Using an analytical instrument that couples dynamic light scattering (DLS) and Raman spectroscopy into a single platform provides a convenient tool for probing the size, structural properties and quality of SWNTs. It is a convenient and powerful tool for the analysis of commercial batches of carbon nanotubes as well as a means for the characterization of material generated from new manufacturing processes. Additionally, the capabilities of this instrument will be of significant value for the study of many other types of nanomaterials and biopharmaceuticals and these topics will be the subject of future application notes.

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