Discover the Raman Advantage!

Carbon-based tubular nanostructures have received much attention in the last few years. Early in their discovery they were simple laboratory curiosities with promising applications. They are now finding use in practical applications for electronic devices and composite materials. Carbon nanotubes (CNTs) are hexagonal lattices of carbon atoms rolled into single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs). The structure, topology, and size of CNTs are a source of their outstanding mechanical and optical properties and their electronic behavior. The design of CNTs must be properly controlled and monitored to meet specific customer needs. Raman spectroscopy is a popular technique for determining the diameter distribution, chirality, purity, and architecture of CNTs.

Raman Spectroscopy of CNTs
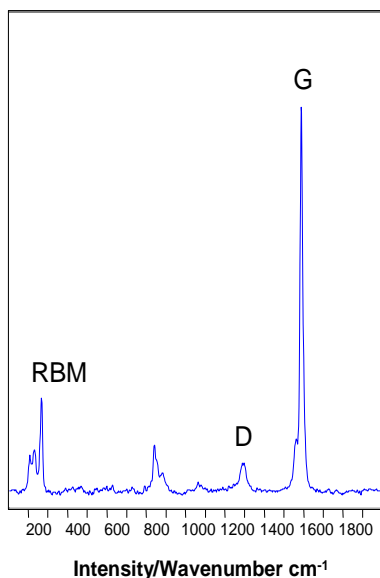The Raman spectrum of a CNT is rich in information (Figure 1).

Figure 1. CNT composite with ExamineR 785

The most prominent Raman features in CNTs are the radial breathing modes (RBMs), the higher frequency D (disordered), G (graphite), and G' (second-order Raman scattering from D-band variation) modes. Although the D, G, and G' modes are found in graphite, the RBM is specific to CNTs and is representative of the isotropic radial expansion of the tube. The RBM frequency is inversely proportional to the diameter of the tube, making it an important feature for determining the diameter distribution in a sample. The RBM bands are a useful diagnostic tool for confirming the presence of CNTs in a sample.

G Band
The G band is a tangential shear mode of carbon atoms (Figure 2) that corresponds to the stretching mode in the graphite plane.
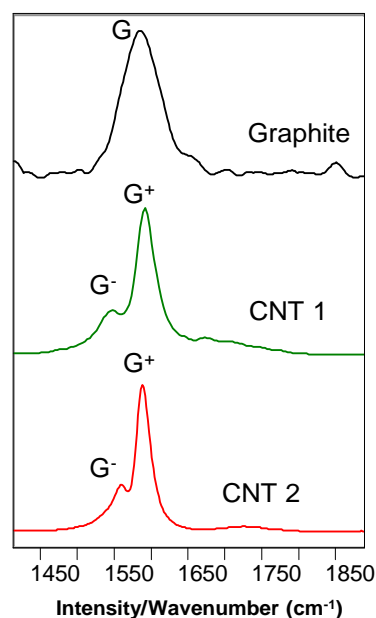

Figure 2. G bands of graphite and two CNT samples

In simple graphite, a single mode is observed at 1580 cm^{-1}. In CNTs this mode transforms into two modes as a result of the confinement of wave-vectors along the circumference. The frequency of the high-energy branch G^+ does not vary with diameter, whereas the lower energy branch G^- becomes softer for smaller diameter CNTs. One of the more intriguing aspects of CNTs is that they can be either metallic or semiconducting with variable and direct bandgap. Vasconcelos and coworkers showed that metallic tubes are easily recognized by the broad and asymmetric line shape of the G^- band. The frequency downshift of the G^- band is particularly strong for metallic tubes, with downshifts of greater than 100 cm^{-1} for smaller diameter tubes, whereas the G^+ frequency remains essentially constant with diameter for metallic and semiconductor tubes.

D Band

The D band is a longitudinal optical (LO) phonon and is known as the disordered or defect mode because a defect is required to elastically scatter in order for the process to conserve momentum. This mode is usually located between 1330 and 1360 cm^{-1} (Figure 3) and has a linear dependence on laser excitation energy. The D band is present in all carbon allotropes, including sp^2 and sp^3 amorphous carbon. In CNTs, this band is activated from the first-order scattering process of sp^2 carbons by the presence of in-plane substitutional hetero-atoms, vacancies, grain boundaries, or other defects, and by finite-size effects. All of these characteristics lower the crystal symmetry of the quasi-infinite lattice.
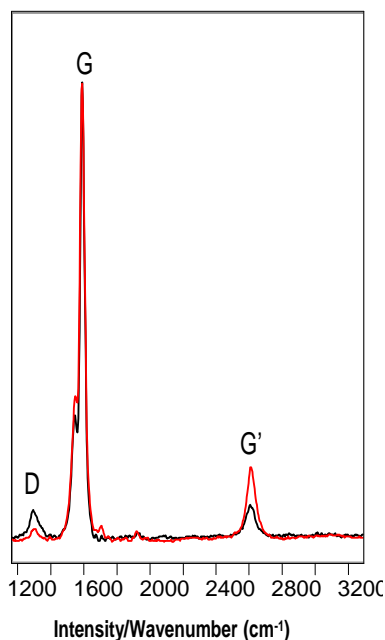

Figure 3. D, G, and G' modes in two different batches of CNTs. The D/G ratio and G' differ in each batch.

When observed in MWNTs the D band has been generally viewed as a defect in the tubes. The quality of a sample has often been evaluated using the D/G band intensities. For high-quality samples without defects and amorphous carbon, the D/G ratio is often less than 2 %. The D-band width for CNTs is generally 10 to 20 cm^{-1}.

G' Band

The G'-band frequency is close to twice that of the D-band and is found from 2500 to 2900 cm^{-1} (Figure 3). This is a second-order process from two zone

boundary LO phonons. The G' band is an intrinsic property of the nanotube and graphite, and present even in defect-free nanotubes for which the D band is completely absent.

RBM Mode

The RBM mode is a confirmation for the presence of CNTs in a sample, since it is not present in graphite. This mode is located between 75 and 300 cm^{-1} from the excitation line, and is associated with the symmetric movement of carbon atoms in the radial direction. The RBM frequency is inversely proportional to the nanotube diameter with the relationship:

$$\omega_r \text{ (cm}^{-1}) = 224 \text{ (cm}^{-1}) / d_t \text{ (nm)}$$

Tube diameters between 0.8 and 1.3 nm give nearly identical results. Most single-grating Raman spectrometers have cutoff frequencies between 100 and 120 cm^{-1}, which restricts the range of tube diameters smaller than 2 to 2.5 nm. Larger tubes can be measured with high Rayleigh rejection multi-grating systems that allow frequencies of less than 100 cm^{-1}. Due to the resonance behavior of the Raman intensity, several laser lines should be used to determine the extent of diameter distribution (Figure 4).
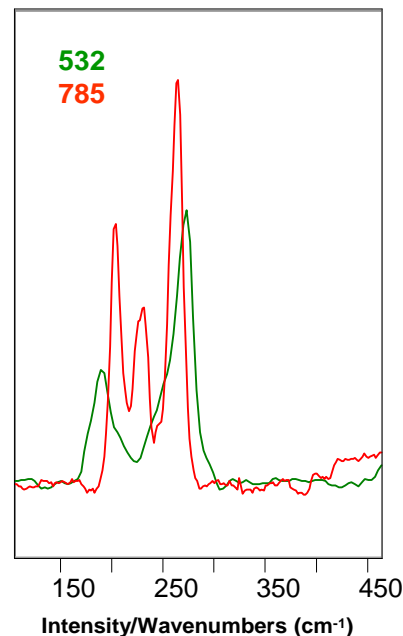

Figure 4. RBM region with ExamineR 532 and 785

Several groups have plotted the excitation energy versus the RBM frequency to form the Raman equivalent of the Kataura plot. A summary of the transition energies has been used to separate RBM signatures of metallic from semiconductor CNTs.

Influence of Excitation Frequency

The choice of laser excitation has little influence on Raman shifts, but most CNT bands are attributed to resonance Raman conditions. That is, the laser energy is resonant with an electronic transition. Scanning the laser energy through an optical resonance can yield the resonance profile for a give phonon mode, and this has proven most useful for full characterization of the RBM modes. Furthermore, this has been shown to provide information about the metallic and semiconductor attributes of a sample to form the Raman equivalent of a Kataura plot (Figure 4).

Laser Power Heating

It is relatively easy to unintentionally overheat a CNT sample. A substantial amount of energy is focused on a small volume, especially under conditions of a high numerical aperture objective. Switching wavelengths has shown to reduce sample burning, and we have determined that powers less than 5 mW are specified for most CNT samples. A high collection throughput spectrometer is necessary to collect signal on low levels of laser power. Composite CNTs and liquid CNT suspensions allow significantly higher laser powers without burning the sample.

Impure nanotubes are more susceptible to laser heating. Evidence of optical heating of the samples has been observed by shifts in the G band to higher frequencies and disappearance of the D band. Granular nanotubes with a significant amount of amorphous carbon tend to heat easily and evidence of their heating has been observed with very large baseline fluctuations while analyzing in continuous mode.

Summary

Raman spectroscopy provides a plethora of information on CNTs. Raman has been shown to determine the presence of CNTs in a sample with evidence of the RBM bands. A multi-laser excitation system provides the metallic and semiconductor characteristics, diameter and chiralities of the tubes, which are highly dependent upon the resonance behavior of the RBM modes and G^- downshifts. The D and G' modes have provided information on defects or purity of the CNTs.

The choice of a Raman spectrometer with attenuated laser powers will help optimize the sensitivity of the Raman signal without sample heating. DeltaNu's free-space design spectrometers allow for very high throughput collection under conditions of low laser power.

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