

Rapid Quality Screening of Carbon Nanotubes with Raman Spectroscopy

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Key Words

- Carbon Nanotubes
- D-band
- G-band
- 2D-band
- G'-band
- Purity
- Quality
- Screening

Introduction

Carbon nanotubes are becoming available at commercially attractive prices, with a number of products incorporating nanotubes already available on the market today. As the quantities of carbon nanotubes being produced and used in commercial products ramps up, it becomes more and more important to have a quick means of verifying the quality of the material. Raman spectroscopy is one method that has become quite popular for this application. Raman measurements are fast and require minimal sample preparation. Thermo Scientific DXR Raman systems are ideally suited for this analysis because of their ease of operation and precise control of measurement parameters.

Measuring Quality – The D-band/G-band Ratio

Numerous publications discuss using Raman spectroscopy to measure the quality or purity of carbon nanotubes through the use of the ratio of the intensity of the D-band ($\sim 1350\text{ cm}^{-1}$) to the intensity of the G-band ($\sim 1582\text{ cm}^{-1}$) as the metric. In some cases variations on this basic scheme are used in which the intensity of the G'-band ($\sim 2700\text{ cm}^{-1}$) is used in place of the intensity of the D-band.

The G-band is the primary Raman active mode in graphite and it provides a good representation of the sp^2 bonded carbon that is present in planar sheet configurations which include the sp^2 bonded carbon of carbon nanotubes. The D-band, known as the disorder or defect mode, originates from edge configurations in graphene where the planar sheet configuration is disrupted. This mode is exhibited on the edge of a graphene sheet or the open end of a carbon nanotube, where you have defects in the tube, and sometimes you will also see some sp^2 bonded amorphous carbon contributing to this band. The G'-band, which is also known as the 2D-band, is an overtone mode of the D-band, although its intensity does not necessarily track with the intensity of the D-band and sometimes it can be more sensitive or less sensitive than the D-band to specific changes in the sample. For example, the G'-band is generally much less sensitive to length of nanotubes than the D-band. All of these bands are resonant enhanced, which means that they are considerably more intense than you would otherwise expect due to resonant coupling with electronic transitions.

In most applications where this approach is being used to measure quality, the D-band/G-band ratio is used only to compare a sample against a reference standard rather than to provide an actual quantitative measure of quality or purity. However, there are a few published examples

in which this metric has been used to provide an actual measurement of carbonaceous purity by preparing a set of calibration standards and referencing the samples to the calibration set. In most of the cases though, this metric is only used to compare to a known good reference standard material. This reference material may be established as a known good material either by extensive characterization with other techniques such as TEM and TGA, or by simple empirical observation that material of this quality produces the desired properties in the end product. If the D-band/G-band intensity ratio in the sample is greater than the same ratio in the spectrum of the reference material, then the material is flagged for closer examination.

Speed of Analysis

The primary reason why Raman spectroscopy is used for these measurements is the speed of analysis. The combined measurement time and sample preparation time are much shorter compared with most other techniques used for this type of characterization. Typical measurement times range from as little as 5 seconds for high density samples to as much as a few minutes for loosely packed powder samples. Samples are run neat, and in terms of sample preparation, typically a small quantity of the material is simply placed on a glass slide and compressed with another glass slide to increase the density. In some cases, where the material is already in solution, the solution may be cast onto a glass slide and allowed to dry. Usually sample preparation takes only a few minutes.

Limitations of the Analysis

While the analysis is very quick and convenient, there are limitations that are important to understand before putting the method into practice. We have already discussed the origins of the vibrational modes underlying these bands. Considering this, it follows that the conditions that would contribute to a higher intensity D-band are a higher concentration of amorphous material, nanotubes in which defects are more prevalent, and shorter tubes where the edge configuration represents a higher percentage of the overall material. In general, singlewall carbon nanotubes (SWCNT) will have much weaker D-bands than multiwall carbon nanotubes (MWCNT). It is also worth noting that while the analyst will often see large differences in the intensity of the D-band when comparing different multiwall tubes with different numbers of concentric layers and different outer diameters, the D-band/G-band ratio will not

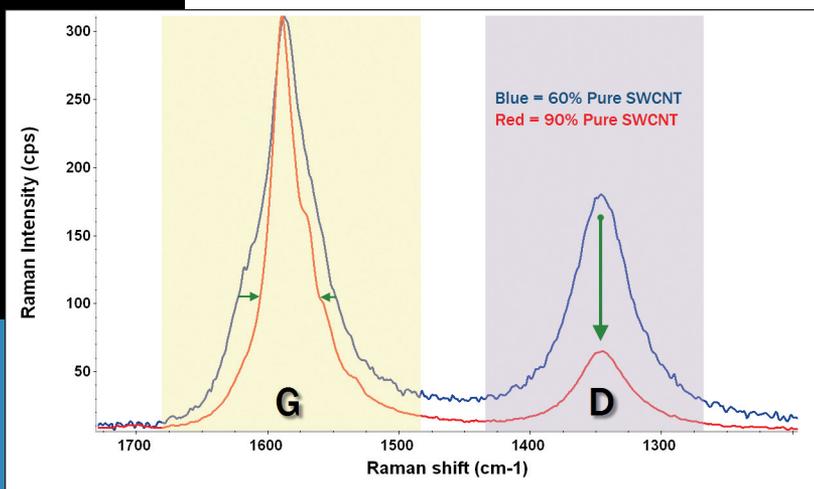


Figure 1: Comparison of the Raman spectra of 60% and 90% pure single-wall carbon nanotubes

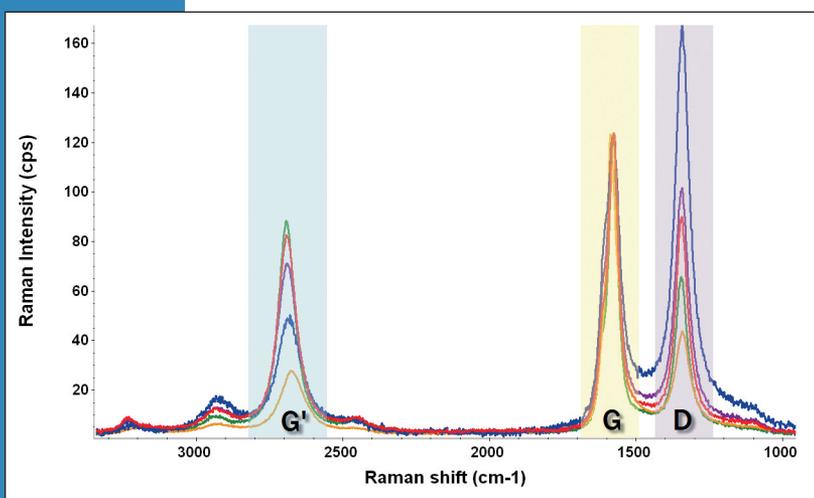


Figure 2: Raman spectra of 95% pure multiwall carbon nanotubes of different diameters ranging from < 8 nm to > 50 nm measured with 0.5 mW of excitation laser power

always correlate neatly with the outer diameter size of these tubes. Figure 1 provides an example of how carbonaceous purity in SWCNT can impact this ratio. Figure 2 provides an example of how the number of layers in MWCNT can impact the ratio.

With so many different attributes of the nanotube contributing to this band, it is not really possible to put a number representing quality or purity (e.g., 95% defect free or 95% pure) on any random sample of nanotubes based on this metric alone. As has already been mentioned, authors have reported that they have been able to successfully assign a purity value based on this approach, but in those cases they have confined their analysis to a highly uniform production stream where much of the potential variability is tightly controlled. If your samples do not fall into this category, it is probably not realistic to expect high accuracy quality or purity measurements as the differences due to length and diameter will likely be at least as significant as the differences due to defect level or purity. However, despite this limitation, this is still a very useful industrial measurement and it is being used routinely in a great number of facilities around the world today. The reason for this is that if you are monitoring production line quality or the quality of incoming materials, most of the attributes that contribute to the D-band represent something that is undesirable in the product, so even if you can not immediately pinpoint which attribute has changed, the fact that there has been a change in the D-band/G-band ratio can be a good indicator that there is a problem of some sort requiring closer examination. The speed of the analysis also makes it very attractive as a quick screening methodology.



Figure 3: Thermo Scientific DXR Raman microscope

Instrumental Considerations

Varying sample attributes are not the only sources of variation in this measurement. The measurement can also be very sensitive to certain measurement parameters. The first of these parameters is excitation laser frequency. Since these bands are resonant, changing the excitation laser frequency can have a dramatic effect on the spectrum. It is therefore very important that when implementing this method you select an excitation laser frequency and continue to use the same frequency for all measurements. Usually this is a 532 nm or a 633 nm laser. Both provide very good results.

The other measurement parameter deserving of a special mention is laser power. While nanotubes themselves are generally not damaged by the excitation laser, nanotubes do absorb a great deal of laser energy, and this produces quite a bit of heat. One danger here is that the heat may damage surface modifications that have been made to the nanotubes or other less durable materials. The second concern with respect to laser power is that the Raman spectrum of nanotubes is very sensitive to temperature. This means that as the laser power is changed you will see significant changes in the spectrum and the D-band/G-band ratio. To limit variation in the measurement, it is very important to maintain the laser power at a constant level. Generally keeping the laser power fairly low avoids laser damage. Even if the laser power is maintained at a stable level, there is more fluctuation in the temperature when using a higher laser power, resulting in more variation in the measurement. By maintaining the laser power at a low level, typically between 0.1 mW and 0.5 mW, very little heat is generated making it easier to maintain a stable temperature.

The need to maintain laser power at a low and very stable level makes Thermo Scientific DXR Raman systems ideally suited for this analysis, as they incorporate a laser power regulator that actively monitors and maintains laser power to very precise levels at all times.

Conclusions

The quality of carbon nanotubes in production is critical to obtaining the desired performance in end products. Having a quick method to screen nanotubes for quality can be very valuable in both production and research environments. Raman spectroscopy offers this capability. Raman measurements are very fast, require almost no sample preparation, and offer a great deal of sensitivity to attributes in carbon nanotubes related to quality and purity, making Raman an ideal technique for quick quality screening of nanotubes. The Thermo Scientific DXR Raman instrument is ideally suited for this analysis because of its simplicity in operation and maintenance, precise control of laser power, and high sensitivity even when using low laser power. Every lab that is interested in monitoring the quality of carbon nanotubes will benefit from having access to a Thermo Scientific DXR Raman instrument.



Figure 4: Thermo Scientific DXR SmartRaman spectrometer

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