Rapid Determination of Purity of Carbon Nanotubes

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ABSTRACT

Raman spectroscopy can provide for quick screening measurements of the carbonaceous purity of carbon nanotube samples. Carbonaceous purity is a critical parameter for many applications of carbon nanotubes. Raman spectroscopy has been reported many times in the literature as a technique which can be used to quickly measure carbonaceous purity although there are few instances in which details are provided on how the analysis is conducted or where limitations to the analysis are described. The goal of this work is to demonstrate the effectiveness and the speed of the technique for this measurement, as well as to help the reader understand the limitations of the analysis and in which situations it can be applied effectively and in which situations it would not be appropriate.

Keywords: raman, d-band, g-band, nanotube, purity

1 EXPERIMENTAL

All Raman microscopy characterization was performed with a Thermo Scientific DXR Raman instrument configured with a 633 nm excitation laser. The instrument was operated using the Thermo Scientific OMNIC 8 software suite.

2 RESULTS AND DISCUSSION

2.1 Measuring Purity

There are numerous publications which discuss using Raman spectroscopy to measure purity or quality of carbon nanotubes through the use of the ratio of the intensity of the D-band (~1350 cm^{-1}) to the intensity of the G-band (~1582 cm^{-1}) as the metric. In some cases variations on this basic scheme are used in which the intensity of the 2D-band (~2700 cm^{-1}) is used in place of the intensity of the D-band. In most common application of this technique the metric is used only to compare against a reference standard rather than to provide an actual quantitative measure of purity, although there are a few examples in which this metric has been used to provide an actual measurement of 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. If the D/G intensity ratio in the sample is greater than the same ratio in the reference then the material is flagged for closer examination.

2.2 Speed of Analysis

The primary reason why Raman spectroscopy is used for this analysis is the speed of analysis. Both the measurement time and sample preparation time are very fast compared with most other techniques being 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. The samples are run neat. Typically a small quantity of the material is 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.

2.3 Limitations of the Analysis

While the analysis is very quick and convenient, there are limitations to the analysis and it is important to understand these limitations before putting the method into practice. The first step to understanding the limitations of the analysis is to understand the origin of these bands and what is actually represented by them. 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 perfect planar sheets. The D-band originates from edge configurations in graphene where the planar sheet

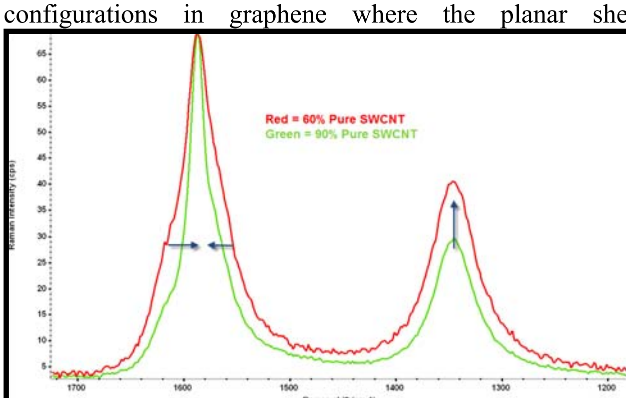

Figure 1. Comparison of the Raman spectra of 60% and 90% pure single-wall carbon nanotubes.

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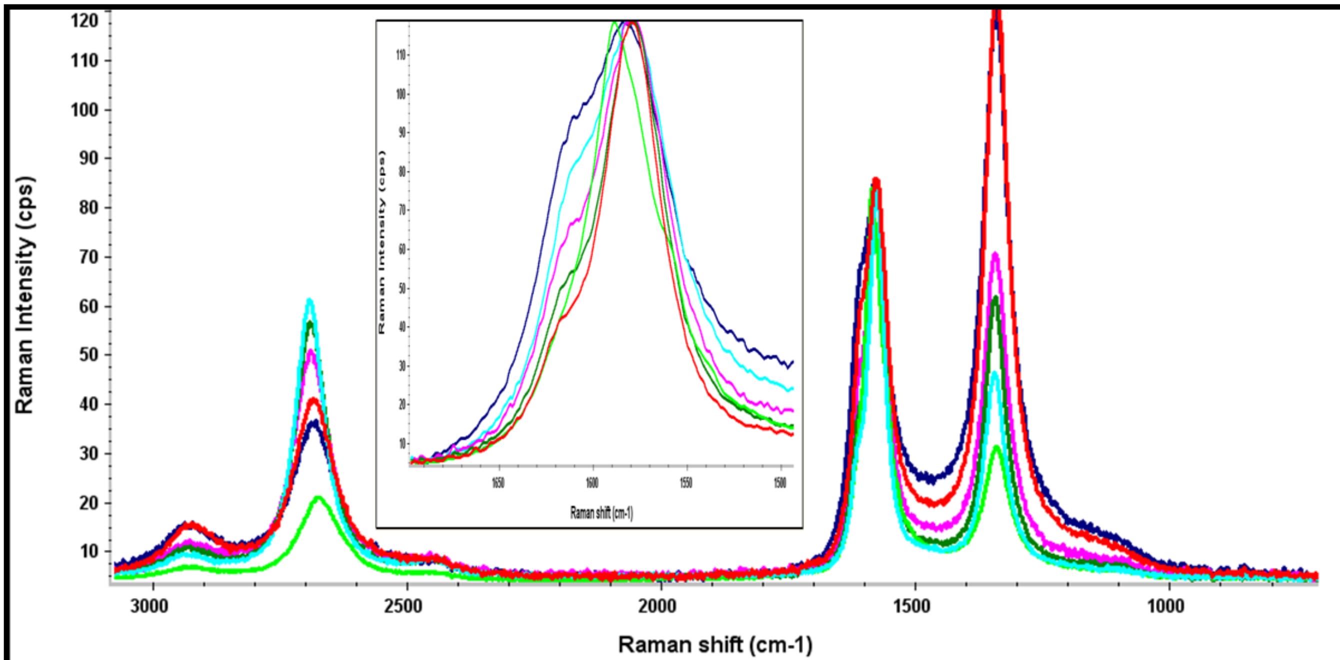

Figure 2. Raman spectra of multiwall carbon nanotubes of different diameters ranging from <8 nm to >50 nm.

configuration is distorted. You will also see some sp2 bonded amorphous carbon contributing to this band. As such the conditions that contribute to a higher intensity D-band are a higher concentration of amorphous material, nanotubes with a higher frequency of defects, shorter tubes where the edge configuration represents a higher percentage of the overall material, and multiwall tubes with a higher number of outer layers. Figure 1 provides an example of how purity can impact this ratio and figure 2 provides and example of how the number of layers in the tube can impact the ratio. With so many different attributes of the nanotube contributing to this band, it is not really possible to put a purity number on any random sample of nanotubes based on this metric alone. As I have already mentioned, people 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 then it is probably not realistic to expect high accuracy purity measurements. However, despite the limitations, 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/G band ratio can be a good indicator that there is a problem of some sort. The speed of the analysis also makes it very attractive as a quick screening methodology.

3 SUMMARY

Raman is a very powerful and valuable technique that can be of great benefit to characterization of carbon nanomaterials. The ratio of the Raman intensity of the D-band to the intensity of the G-band provides a quick method to screen materials for carbonaceous quality although you have to be careful when trying to extract more precise information using this method. Every lab that is monitoring the quality of Carbon nanomaterials will benefit from having access to Raman instrumentation.