

The Importance of Tight Laser Power Control When Working with Carbon Nanomaterials

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Introduction

The field of carbon nanomaterials is growing rapidly. Because of the wealth of information it can provide, Raman spectroscopy is gaining more and more popularity as a characterization tool within this field. However, before getting started in the characterization of carbon nanomaterials with Raman spectroscopy a few facts should first be considered. One of the most important is understanding the impact that excitation laser power has on carbon nanomaterial samples. It is particularly important to have precise control over excitation laser power. Fortunately, Thermo Scientific DXR Raman instruments are equipped with a unique device to provide you with the precise control you need.

Impact of Laser Power

The impact of laser power is two fold. First it is important to be aware that with some materials it is possible to damage or alter the sample with the excitation laser. This damage can be very obvious in extreme cases where the laser burns a hole in the sample; in other cases the damage can be more subtle and if care has not been taken to avoid damaging the sample, it may result in spectra that do not represent the true sample. Such data could easily be

misinterpreted. Figure 1 provides an example of one such situation with a sample of C₆₀ fullerene. Here we can see that the C₆₀ begins to breakdown into other structures, probably amorphous carbon, with as little as 0.5 mW of laser energy applied to the sample. It turns out that C₆₀ is one of the more sensitive carbon nanomaterials, but even when dealing with more laser tolerant materials such as carbon nanotubes, you have to exercise some caution as it is possible that surface modifications to these materials may not be as laser tolerant as the base materials.

The second way that laser power can impact samples of carbon nanomaterials is by changing the temperature of the sample. The Raman spectra of many carbon nanomaterials can be very sensitive to even small temperature changes. Figures 2 and 3 provide two examples of multiwall carbon nanotubes and singlewall carbon nanotubes, respectively, which demonstrate the effect that relatively small changes in laser power can have on the Raman spectra by inducing small temperature changes in the samples. Most carbon nanomaterials are black in color and will absorb significant amounts of visible light. Most of this absorbed energy will be converted to heat, thereby changing the temperature of the sample in the locality where the excitation laser is applied.

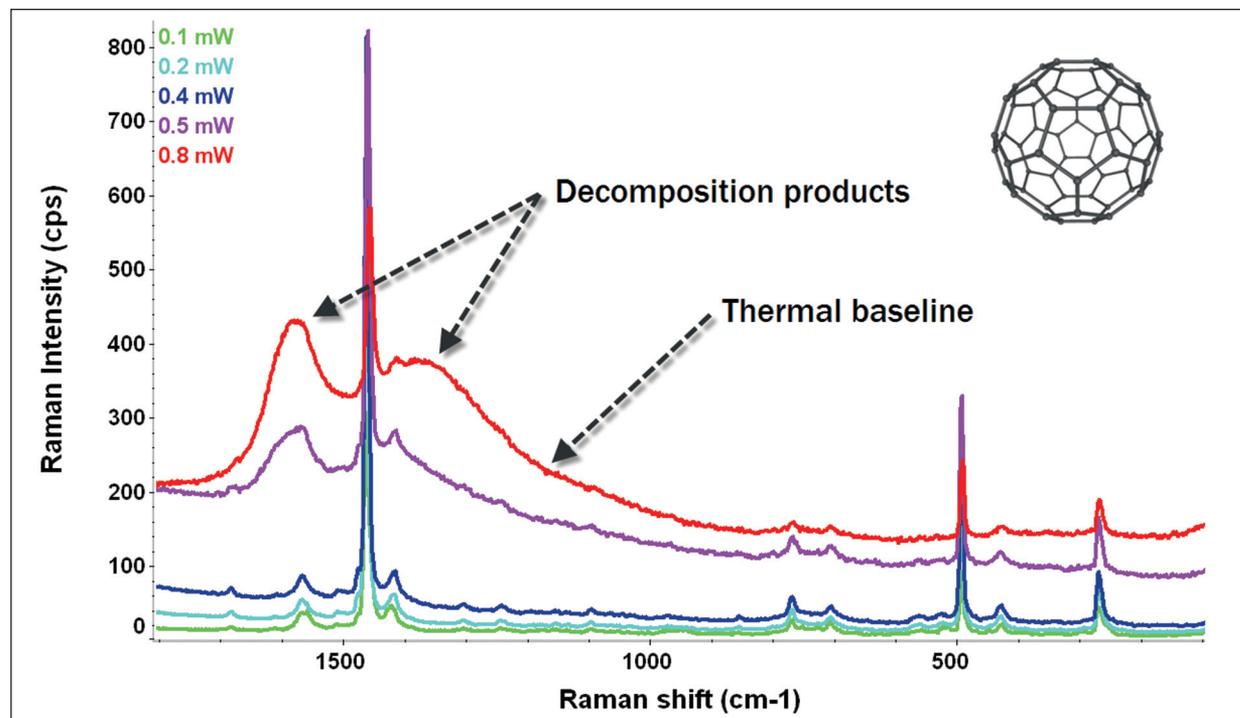


Figure 1: Effect of increasing laser power on C₆₀ (532 nm excitation laser)

Key Words

- Carbon Nanomaterials
- Carbon Nanotubes
- D-band
- G-band
- 2D-band
- Laser Power

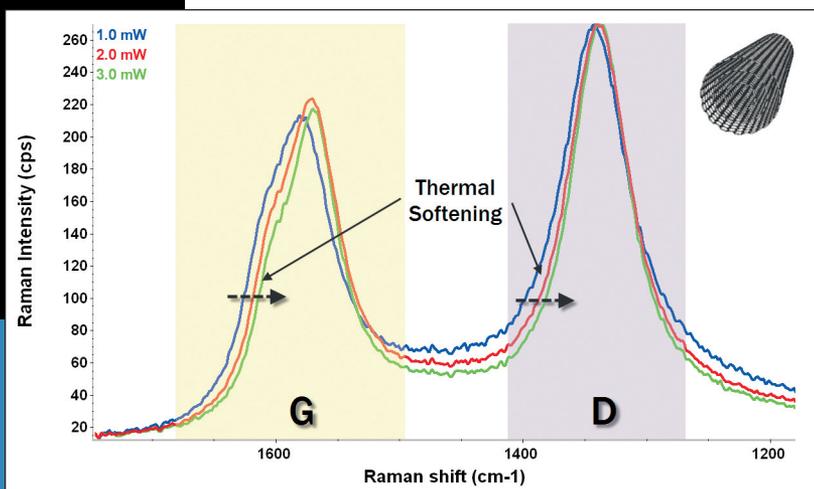


Figure 2: Effect of thermal softening with increasing laser power on multiwall carbon nanotubes (532 nm excitation laser)

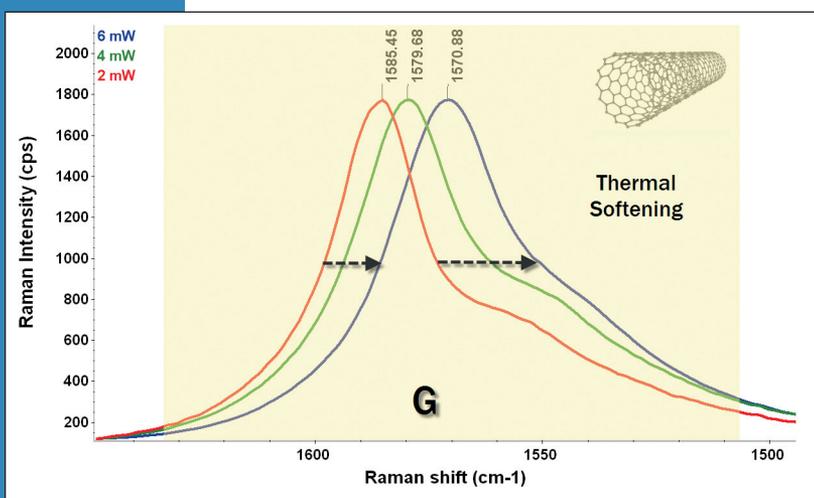


Figure 3: Effect of thermal softening with increasing laser power on singlewall carbon nanotubes (780 nm excitation laser)

In both of these examples we see significant shifts in the G-band, and in the multiwall carbon nanotube example we also see some shifting of the D-band. This is the effect of thermal softening of the planar graphene configuration of the tubes. As the temperature increases because of laser excitation the bonds become somewhat looser, which results in a lower vibrational energy and hence a shifting of the G-band to lower wavenumbers. The band shifts that we can observe here have a significant impact on any attempt to do characterization based on fine interpretation of the Raman spectrum. In some cases they may even be significant with simple quality assessments such as those routinely done by comparing the ratio of the intensity of the D-band to the intensity of the G-band. In the example presented in Figure 2, the D-band/G-band intensity ratio decreases by 6% as we increase the laser power from 1 mW to 2 mW, and then decreases by 3% when we further increase the laser power from 2 mW to 3 mW. This may or not be significant to the quality assessment, depending on how tight the tolerances are, but in any case it certainly magnifies the variation that is present in the measurement.

Solutions

Fortunately there are some relatively simple solutions to controlling these effects. For starters, when beginning to characterize new materials or materials with new modifications, the analyst should always start with very low laser power. If a number of samples of the same material are anticipated, we recommend testing a small area of one sample to check for laser tolerance. Collect spectra at different laser powers to identify how much power can be applied before you begin to see damage in the Raman spectrum. Once you understand the upper limit of laser power that your material can safely handle, then you can move forward with your measurements with confidence.



Figure 5: Thermo Scientific DXR Raman microscope

Once you have worked out the safe limits for your material, it is time to think about controlling any temperature effects that you observe. The approach to controlling temperature effects follows two avenues. The first may sound obvious, but avoid exciting an area of the sample larger than the area over which emissions will be collected and focused on the detector. Any portion of the sample that is exposed to the excitation laser, but is out of the view of the detector, is not generating Raman signal. It is only generating heat at the sample. With Thermo Scientific DXR Raman instruments, the laser spot size on the sample is either matched to the size of the area that the detector sees or is slightly smaller than the area that the detector sees. An optical design such as this coupled with a highly accurate alignment process to insure that the excitation laser spot is always positioned over the area of the sample that the detector sees will minimize sample heating and provide the best control of temperature effects. Thermo Scientific DXR Raman systems also include a patented autoalignment system that insures that these areas are always in close alignment.

The next important factor to managing sample temperature is having very precise control of your laser power at the sample and the ability to adjust that laser power in small increments. Once again Thermo Scientific DXR Raman systems provide exactly what you need. DXR™ Raman systems are equipped with a unique device called a laser power regulator. Unlike simple neutral density filters that are used with most Raman systems, the laser power regulator utilizes a gradient-neutral density filter that can be adjusted with high precision. This is coupled with a laser power meter calibrated to the sample position such that the laser power is actively monitored and adjusted to insure that the set power matches delivered power. This also enables fine control of the laser power to within 0.1 mW

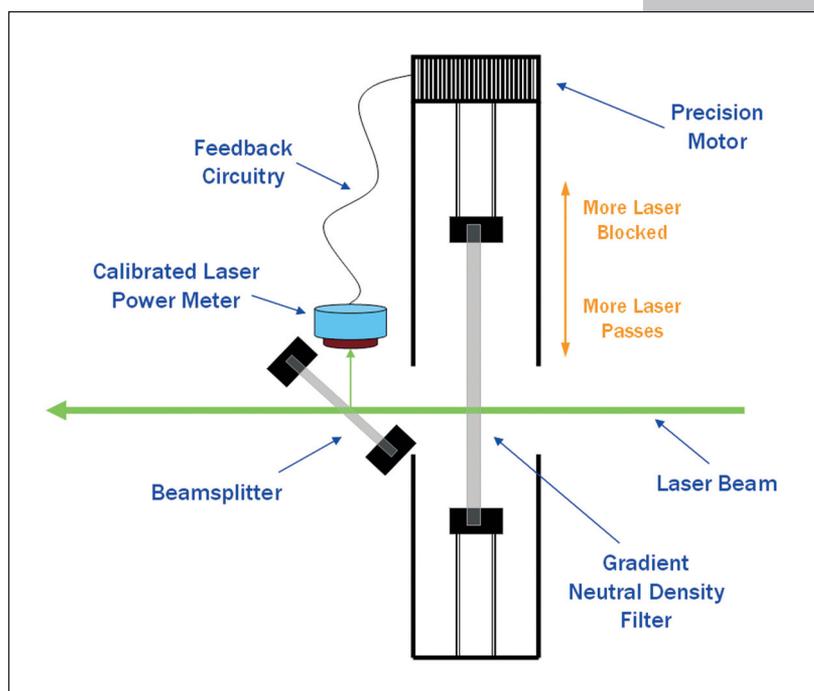


Figure 4: Principle of operation of Thermo Scientific Laser Power Regulator

increments, providing both confidence and a great deal of flexibility to optimize measurement conditions. Figure 4 illustrates the concept of the laser power regulator.

Finally, many carbon nanomaterial samples necessitate operating with very low excitation laser power. Even if a higher laser power does not damage the sample, it is easier to control thermal effects if you reduce the amount of heat generated on the sample. As you increase the laser power, and hence the heat being generated at the sample, you may observe more variability in the spectra due to these



Figure 6: Thermo Scientific DXR SmartRaman spectrometer

temperature effects. If you keep the laser power low and avoid generating a lot of heat, the sample will dissipate the heat more efficiently thereby stabilizing spectral variations. Since we will need to operate with low laser power and consequently low Raman emissions, it is also important to have a system that performs well under these conditions. Again the ability to maintain a system in a well aligned state is going to be key to achieving good sensitivity under conditions of low Raman emissions.

Conclusions

Raman spectroscopy has proven to be a very powerful tool for characterization of carbon nanomaterials; however care has to be taken to properly control the laser power in order to avoid the risk of sample damage, and to avoid the risk of introducing additional variability into the measurement. Thermo Scientific DXR Raman instruments provide an unparalleled level of laser power control and great sensitivity with low laser power combining all the benefits offered by Raman with the precise control over measurement parameters needed for the complete confidence that you want in your results.

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