Carbon Analysis with High Signal-Throughput Portable Raman Spectroscopy

Introduction

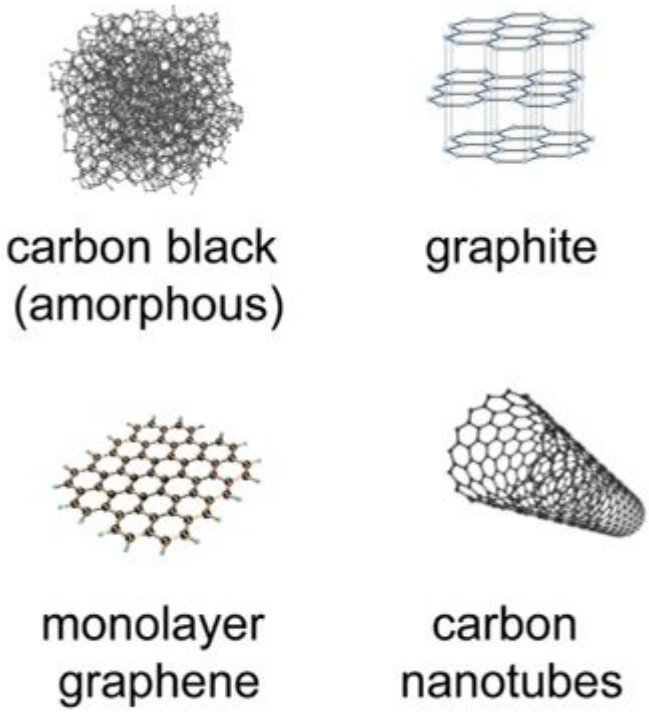

Figure 1. Structure of carbon allotropes.

Carbon nanomaterials such as graphene, graphite, and carbon nanotubes (**Figure 1**) each have unique physical and thermal properties that make them important in industries as varied as battery manufacturing, construction, and sports equipment. As these materials are more widely used in manufacturing settings, the necessity for simple, safe and robust characterization methods grows.

Raman spectroscopy is a valuable tool for characterization of carbon nanomaterials due to its selectivity, speed, and ability to measure samples nondestructively. Raman spectra of carbon materials are typically quite simple, but can reveal a wealth of information about the internal microcrystalline structures based on peak positions, shape, and relative intensity. Raman

spectra graphene-based materials are characterized by three major peaks: the G-band, the D-band, and the 2D-band.

The G-band is present at around 1580 cm^{-1} and represents the graphene in-plane bending motion of the sp^2 hybridized carbon atoms. In high-quality graphene, the G-band is very sharp, indicating high crystallinity. The position of the G-band is also sensitive to the number of graphene layers, but is independent of the laser excitation.

The D-band can be considered as a measure of disorder within a graphene sample. The band is representative of a ring breathing mode for the sp^2 hybridized carbon atoms. For the D-band to be observed in a spectrum of graphene, there must either be a defect in the graphene, or the mode is close to an edge. In pristine graphene, the D-band is not visible. The D-band exhibits dispersive behavior, meaning that it is sensitive to the laser excitation used in the experiment.

The 2D band is an overtone of the D-band, but unlike the D-band it is not required to be close to a defect for activation. The peak shape of the 2D band can be used to determine the layer thickness. Like the D-band, the 2D band is also dispersive, so it will change slightly with a different laser excitation.

Configuration

BWT-840000395 - Raman Probe Holder
Probe holder for use with B&W Tek's lab-grade Raman probes. Provides manual coarse and fine XYZ adjustments.

BWT-840000609 - Enclosure for Raman sampling system
Enclosure for Raman sampling system (i.e. microscope, probe holder) used to eliminate direct ocular and/or skin exposure from the laser emission. The enclosure is ergonomically designed to facilitate sample loading and system operation. For use with 532, 785 and 1064 nm wavelengths.

Experiment

An i-Raman® Prime 532H system was used for all measurements of graphene-based materials. The system has a 532 nm laser, which is the laser wavelength commonly chosen for Raman measurements of carbon.

The i-Raman Prime is a low-noise, high signal-throughput and fully integrated Raman system with an embedded tablet computer. A probe holder was used for all measurements to support the fiber optic probe. An enclosure system is also available, making the otherwise class 3b laser as a class 1 laser that is safe for a manufacturing floor. Typical laser power used is ~34 mW, and acquisition times range from 30-90 s.

Table 1. Configuration for measuring carbon materials

System model	i-Raman® Prime 532H
Laser wavelength	532 nm
Accessories	Probe holder BAC150B
	Video microscope BAC151C-532 (optional)
	E-grade probe upgrade for SWCNTs (optional)
Software	BWSpec®

Raman spectra of carbon nanomaterials

The D-band represents the degree of disorder within a graphene sample, while the G-band represents the level of structural order. Hence, the calculated ratio of the D and G-band intensities (I_D / I_G) can be used as a semi-quantitative parameter for determining the quality of a graphene sample. The I_D / I_G increases as structural disorder within a sample increases. This I_D / I_G parameter represents a quick quality-control parameter that can be used as a Pass/Fail test in manufacturing settings.

Figure 2 shows the Raman spectra of some carbon nanomaterials. A spectrum of pristine graphene (**red spectrum**) contains only the G-band and the 2D-band; there is no D-band present. Furthermore, the ratio of the intensity of the 2D band to the intensity of the G-band (I_{2D} / I_G) 2. The spectrum of graphite (**green spectrum**) is characterized by a widened and asymmetrical 2D band, and the I_{2D} / I_G is much lower. Spectra from carbon nanotubes (**black spectrum**), which are rolled up tubes of graphene, exhibit a slightly split G-band.**[1]** The curvature of single-walled carbon nanotubes (SWCNTs) splits the G-band into two degenerate modes, G^+ and G^- . Carbon black (**blue spectrum**), which has the least structural order,

exhibits a strong D-band, and therefore a high I_D / I_G. It is worth noting that with a different laser then the 532 nm laser used for these measurements, the position of the D-band and 2D band will change slightly due to their dispersive nature.

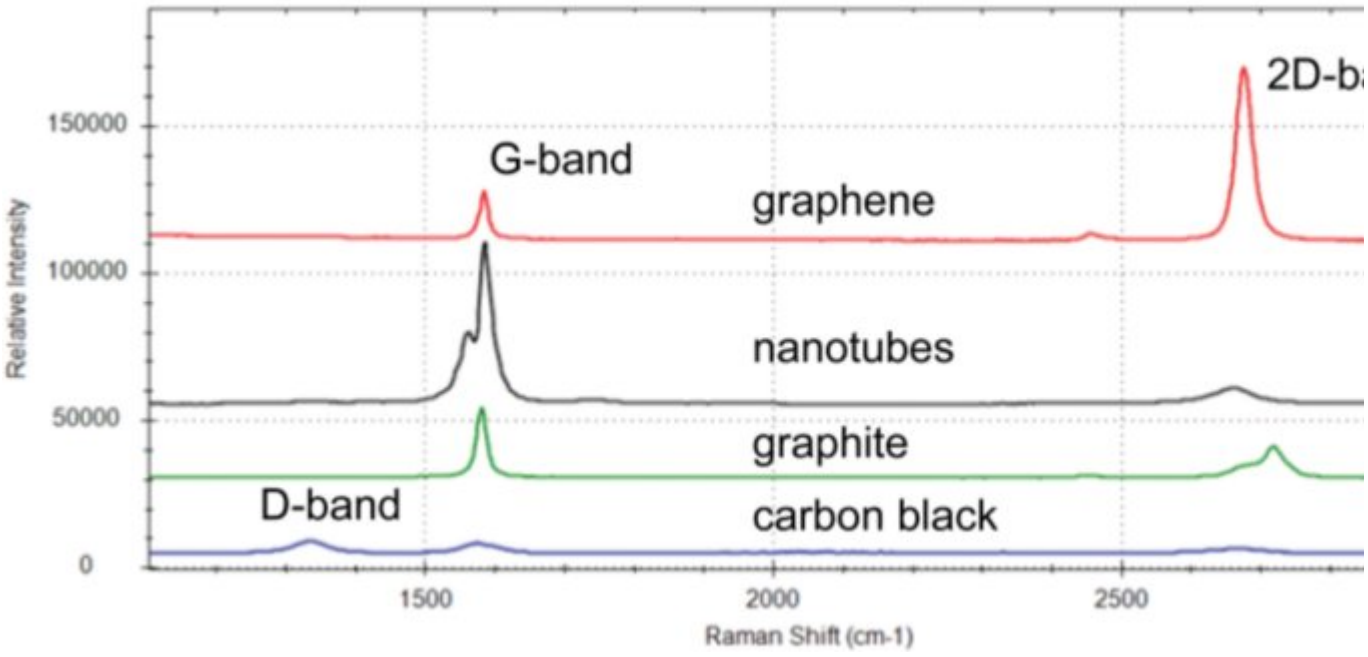

Figure 2. Raman spectra of graphene (red), carbon nanotubes (black), graphite (green), and carbon black (blue).

Determination of ID / IG

Guidelines for calculating ID / IG with Raman spectroscopy are documented in ASTM E3220-20 Standard Guide for Characterization of Graphene Flakes.**[2]** Spectra should be baseline corrected prior to finding peak intensity. For the spectra in **Figure 3**, a baseline removal algorithm was applied to the data in the BWSpec software. After baseline removal, the peak intensities of the D-bands and G-bands of the spectra are measured. Then the I_D / I_G can be calculated. The BWSpec software can be configured to report the I_D, I_G, and calculate the derived I_D / I_G from a collected spectrum. The calculations can be exported to a table for easy reporting. **Table 2** shows the table that is generated in the software.

Table 2. Measured I_D, I_G, and calculated I_D / I_G from BWSpec software

Data source	D-band	G-band	D/G
Carbon black_1	1276.1205	1780.7942	0.7166
Carbon black_2	2184.0956	3037.7693	0.7190
Carbon black_3	851.1320	1457.8104	0.5838
Carbon black_4	1318.5770	2123.2700	0.6210
Carbon nanofiber_1	5179.8889	3289.7727	1.5745
Carbon nanofiber_2	2786.3214	5583.2101	0.4991

In **Figure 3**, the nanofiber spectra are characterized by intense D-bands at around 1350 cm^{-1} and some asymmetry in the G-bands. The I_D / I_G of spectrum (a) is particularly high, indicating that there is a high degree of structural disorder within that nanofiber sample.

The spectra from the carbon black samples are categorized by broad D-bands and G-bands, indicating very low crystallinity within the samples. The measured I_D / I_G for the carbon black samples are all above 0.5, indicating structural disorder within the structure of the sample. This I_D / I_G can be used as a quick quality-control test of manufactured graphene, graphite, carbon nanotubes, and carbon black powder, either as an offline or at-line measurement.

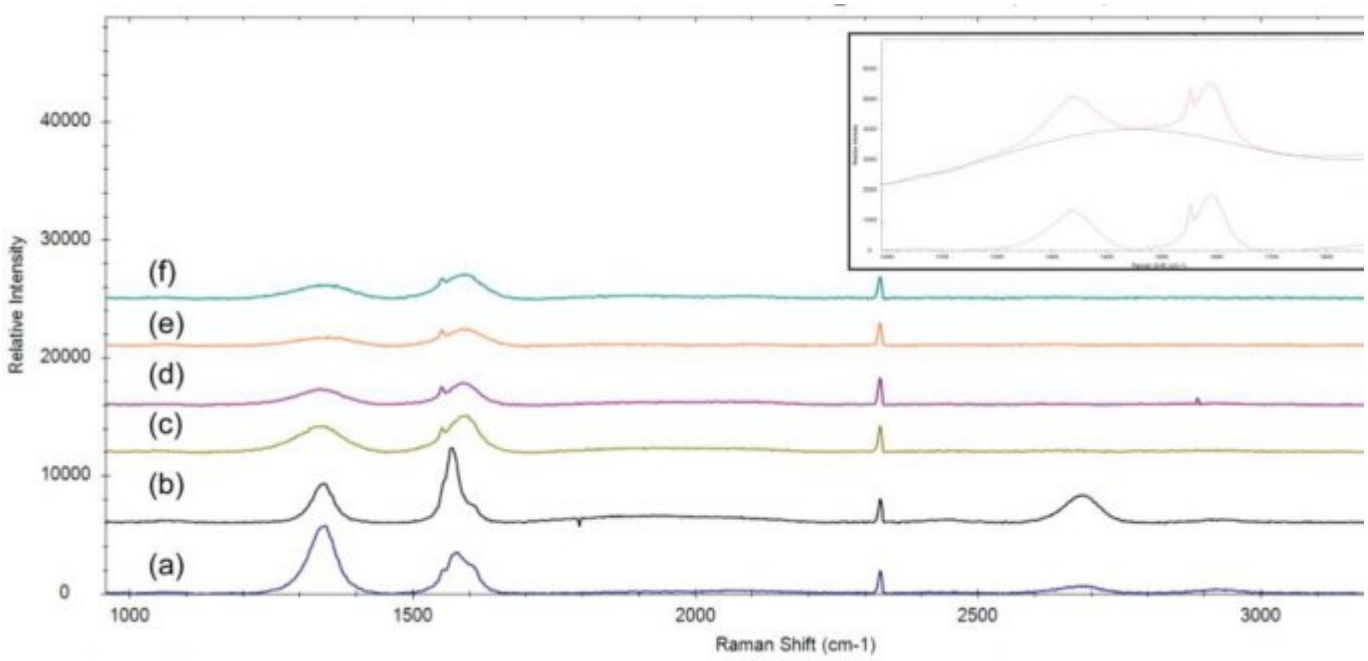

Figure 3. Raman spectra of carbon nanofibers (a,b) and carbon black powders (c-f). The insert shows an example of the baseline correction that was applied to all of the data. All spectra are manually offset for clarification. Note: sharp peaks at ~1550 cm-1 and ~2300 cm-1 are attributed to atmospheric oxygen and nitrogen, respectively.

Conclusion

Raman spectroscopy has grown to be a valuable technique for characterization of carbon nanomaterials. Carbon spectra are quite simple and often only characterized by three peaks. The peak intensities, shapes, and positions reveal information about the internal crystallinity of the sample. The ratio of the intensity of the D-band to the intensity of the G-band acts as a simple indicator of structural disorder or a sample. This I_D / I_G of a sample can be used by researchers and manufacturers to characterize their carbon nanomaterials.

References

1. A. C. Ferrari. *Solid State Communications*. **143**, 47–57 (2007)
2. ASTM E3220-20, Standard Guide for Characterization of Graphene Flakes, ASTM International, West Conshohocken, PA, 2020, www.astm.org

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