Characterization of carbon materials with Raman spectroscopy

Following the guidelines of ASTM E3220

Carbon nanomaterials such as graphene, graphite, and carbon nanotubes each have unique physical and thermal properties that make them important in industries as varied as battery manufacturing, construction, and sports equipment. The necessity for simple, safe, and robust characterization of these materials grows as they are more widely used in manufacturing settings.

Raman spectroscopy is a valuable tool for the characterization of carbon nanomaterials due to its selectivity, speed, and ability to measure samples nondestructively. Carbon materials typically exhibit simple Raman spectra, but they contain a wealth of information about internal microcrystalline structures in peak position, shape, and relative intensity.

INTRODUCTION

Raman spectra of graphene-based materials, like those in **Figure 1**, are characterized by three major peaks: the G-band, the D-band, and the 2D-band.
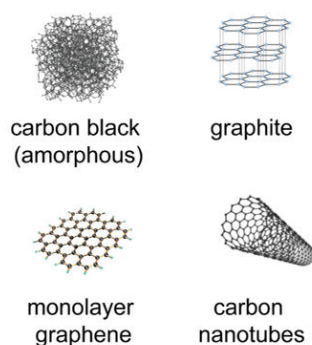
Figure 1. Structure of different carbon allotropes.

The G-band appears near 1580 cm^{-1} and represents the in-plane bending motion of doubly bonded carbon atoms. In high-quality graphene, the G-band is very sharp, indicating a high degree of crystallinity. The position of the G-band is sensitive to the number of graphene layers but is independent of laser excitation.

The D-band indicates disorder within a graphene sample. This band arises from a ring breathing mode for doubly bonded carbon atoms. In pristine graphene, the D-band is not visible. The D-band is observed when there is a defect in the graphene, or the mode is close to an edge. The D-band exhibits dispersive behavior, meaning that it is sensitive to the laser excitation wavelength used in the experiment.

The 2D-band is an overtone of the D-band, and the peak shape of the 2D-band can be used to determine layer thickness. Like the D-band, the 2D-band is dispersive and will change slightly with laser excitation.
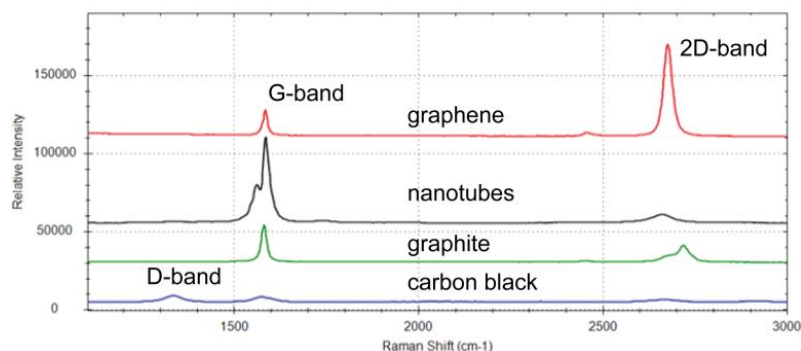
RAMAN SPECTRA OF CARBON NANOMATERIALS

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

Figure 2 shows Raman spectra from different carbon nanomaterials. Pristine graphene (red) contains only G- and 2D-bands; there is no D-band. The ratio of the intensity of the 2D-band and the intensity of the G-band (I_{2D}/I_G) ≈ 2. Graphite (green spectrum) is characterized by a widened and asymmetrical 2D-band, and the I_{2D}/I_G ratio is much lower. 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 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 has a high I_D/I_G. Note that laser excitement at a wavelength other than 532 nm will cause the slight shifts in the position of the D-band and 2D-band, due to their dispersive nature.

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

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 measurement of carbon. The i-Raman Prime is a low-noise, high-throughput, fully integrated Raman system with an embedded tablet computer.

A probe holder (BAC150B) was used for all measurements to support the fiber optic probe. An enclosure system (BAC152C) is available to achieve class 1 laser safety for a manufacturing floor. Typical laser power used is ~34 mW and acquisition times range from 30–90 s.

Table 1. Experimental parameters.

Equipment	Acquisition settings	
i-Raman Prime 532H	Laser Power	100%
Probe holder (BAC150)	Int. time	30–90s
BWSpec Software	Average	1

Determination of I_D/I_G

Guidelines for calculating I_D/I_G are documented in ASTM E3220 Standard Guide for Characterization of Graphene Flakes [2]. Spectra undergo baseline correction prior to peak intensity determination. For the spectra in **Figure 3**, a baseline removal algorithm was applied to data in the BWSpec software. The sharp peaks at ~1550 cm^{-1} and ~2300 cm^{-1} are attributed to atmospheric oxygen and nitrogen,

respectively.

After baseline removal, peak intensities of spectral D- and G-bands are measured and I_D/I_G can be calculated. The software can be configured to automatically report I_D, I_G, and derived I_D/I_G from a collected spectrum. The results can be easily exported to a report. **Table 2** shows the table that is generated in the software.

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Table 2. Measured ID, IG, and calculated ID/IG from BWSpec software. Data sources align with those in Figure 2.

Source	D-band	G-band	D/G
a	2786.3214	1780.7942	0.7166
b	2184.0956	3037.7693	0.7190
c	851.1320	1457.8104	0.5838
d	1318.5770	2123.2700	0.6210
e	5179.8889	3289.7727	1.5745
f	2786.3214	5583.2101	0.4991

In **Figure 3**, nanofiber spectra are characterized by 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 (c–f) are categorized by broad D-bands and G-bands, indicating very low crystallinity within the samples.

Measured I_D/I_G for the carbon black samples are all above 0.5, indicating structural disorder within the sample. I_D/I_G can be used as a quick offline or atline quality control test of manufactured graphene, graphite, carbon nanotubes, and carbon black powder.

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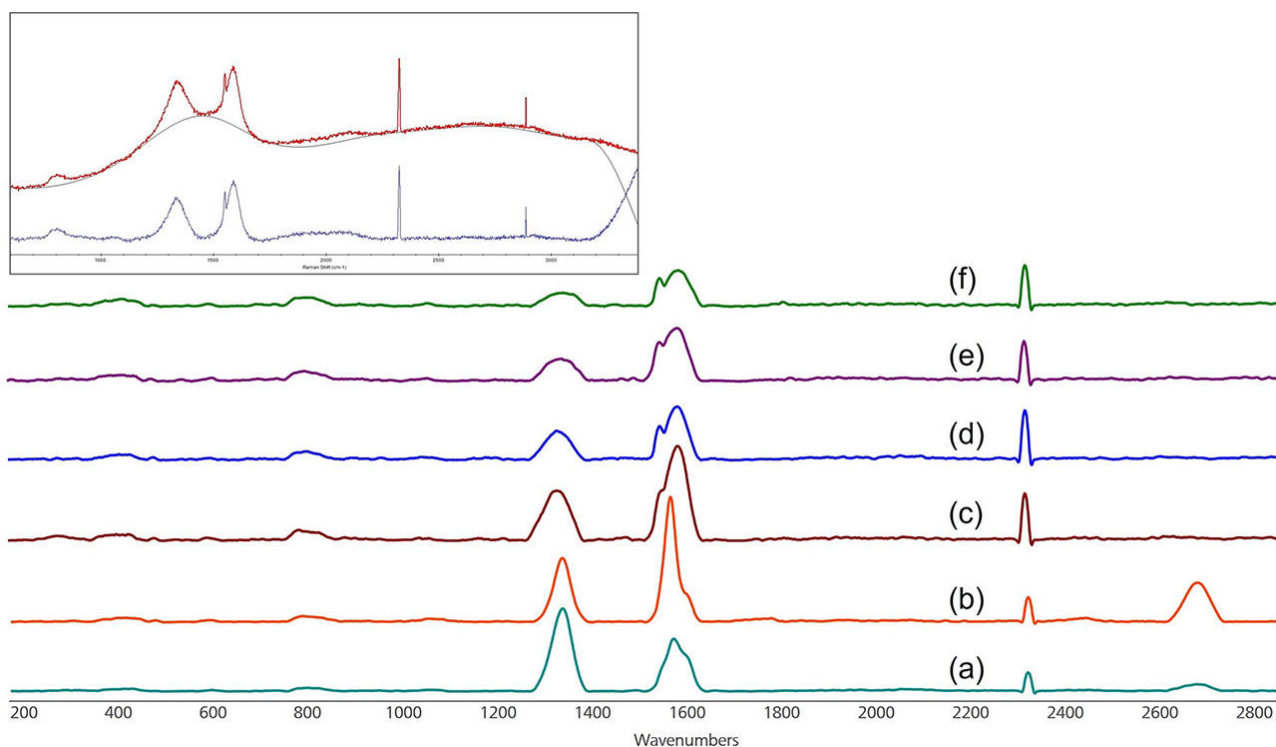
Figure 3. Raman spectra of carbon nanofibers (a,b) and carbon black powders (c–f). The insert shows an example of the baseline correction that was applied to all data. All spectra are manually offset for clarification.

CONCLUSION

Raman spectroscopy is 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.

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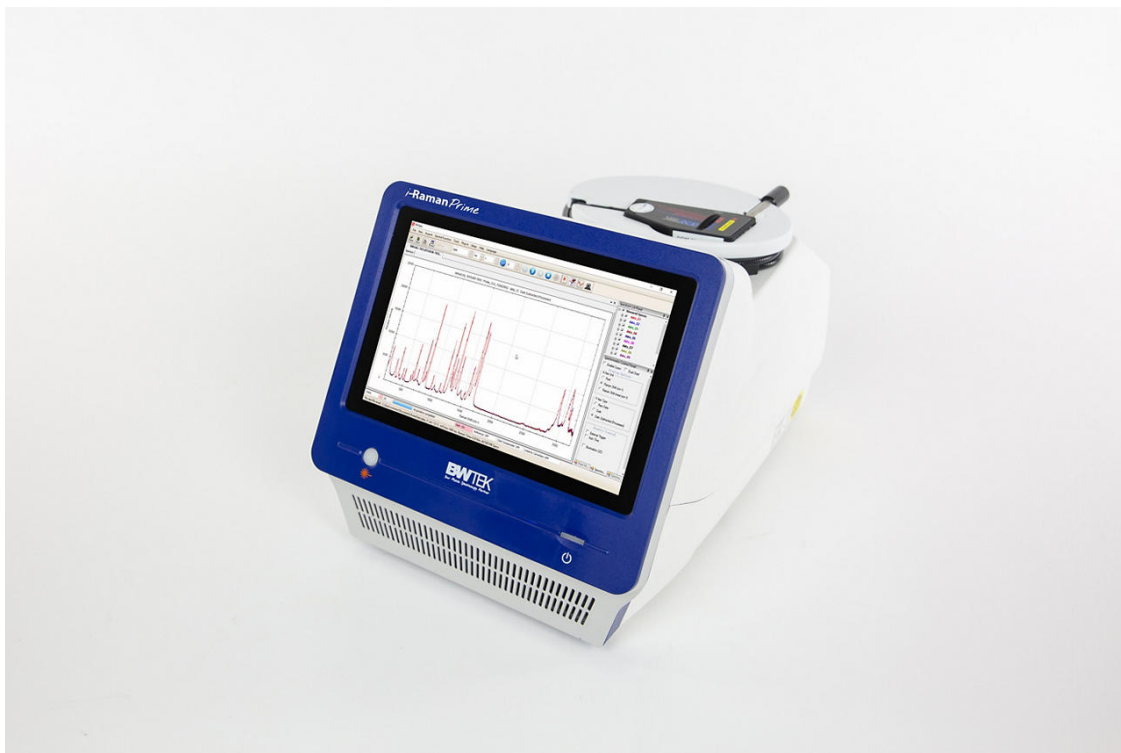
REFERENCES

1. Ferrari, A. C. Raman Spectroscopy of Graphene and Graphite: Disorder, Electron–Phonon Coupling, Doping and Nonadiabatic Effects. *Solid State Communications* **2007**, *143* (1), 47–57. https://doi.org/10.1016/j.ssc.2007.03.052.

2. ASTM International. *Standard Guide for Characterization of Graphene Flakes*; ASTM E3220-20; ASTM International, 2020.

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CONFIGURATION
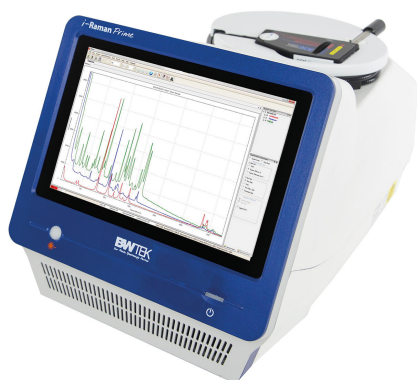
i-Raman Prime 532H Portable Raman Spectrometer

The i-Raman® Prime 532H is a low-noise, high-throughput, and fully integrated Raman system with an embedded tablet computer and a fiber-optic sampling probe. Using a high-quantum-efficiency CCD array detector with TE deep cooling (-25 °C) and high dynamic range, this portable Raman spectrometer delivers research-grade Raman analysis capabilities, including real-time quantitation and identification. The high throughput gives Raman spectra with excellent signal-to-noise ratio, making it possible to measure rapid processes and to measure even the slightest Raman signals, detecting subtle sample differences.

In addition to its portable construction, the i-Raman Prime 532H features the unique combination of wide spectral coverage and high resolution, thus enabling measurements from 150 cm^{-1} to 3400 cm^{-1}. The i-Raman Prime can be battery-operated for easy portability, providing research-grade Raman analysis capabilities for high-precision qualitative and quantitative work wherever needed. The system is optimized for use with our STRaman® technology for analyses through non-transparent packaging.
BWS475-532H-HT

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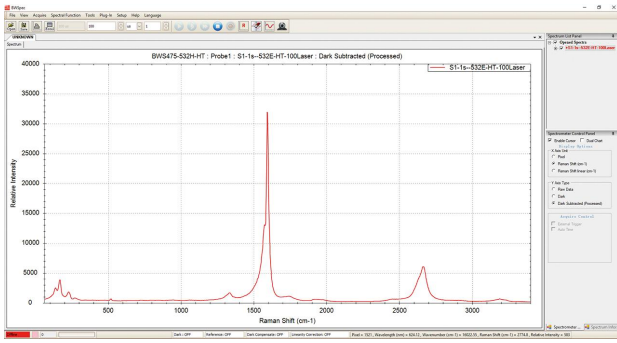
BWSpec Software

BWSpec® is B&W Tek's general spectroscopy software for instrument control and data acquisition, including real-time peak analysis and trending. BWSpec is the operating software included with the purchase of all B&W Tek portable Raman systems and spectrometer products. It is designed with features for broad range applications, performing complex measurements and calculations at the click of a button. It supports multiple data formats and provides the option to optimize measurement parameters, such as integration time and laser output power control. In addition to data acquisition and data processing, it also offers automatic dark removal, spectral smoothing, baseline correction, as well as peak monitoring and trending.

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