# 材料的拉曼光表征

## Following the guidelines of ASTM E3220

**概要**

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.
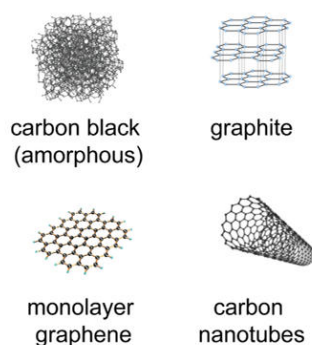
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**Figure 1.** Structure of different carbon allotropes.

## INTRODUCTION

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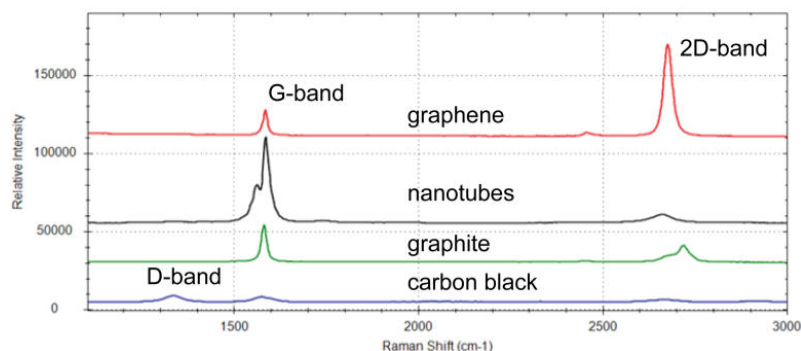
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**Figure 2.** Raman spectra of graphene (red), carbon nanotubes (black), graphite (green), and carbon black (blue).

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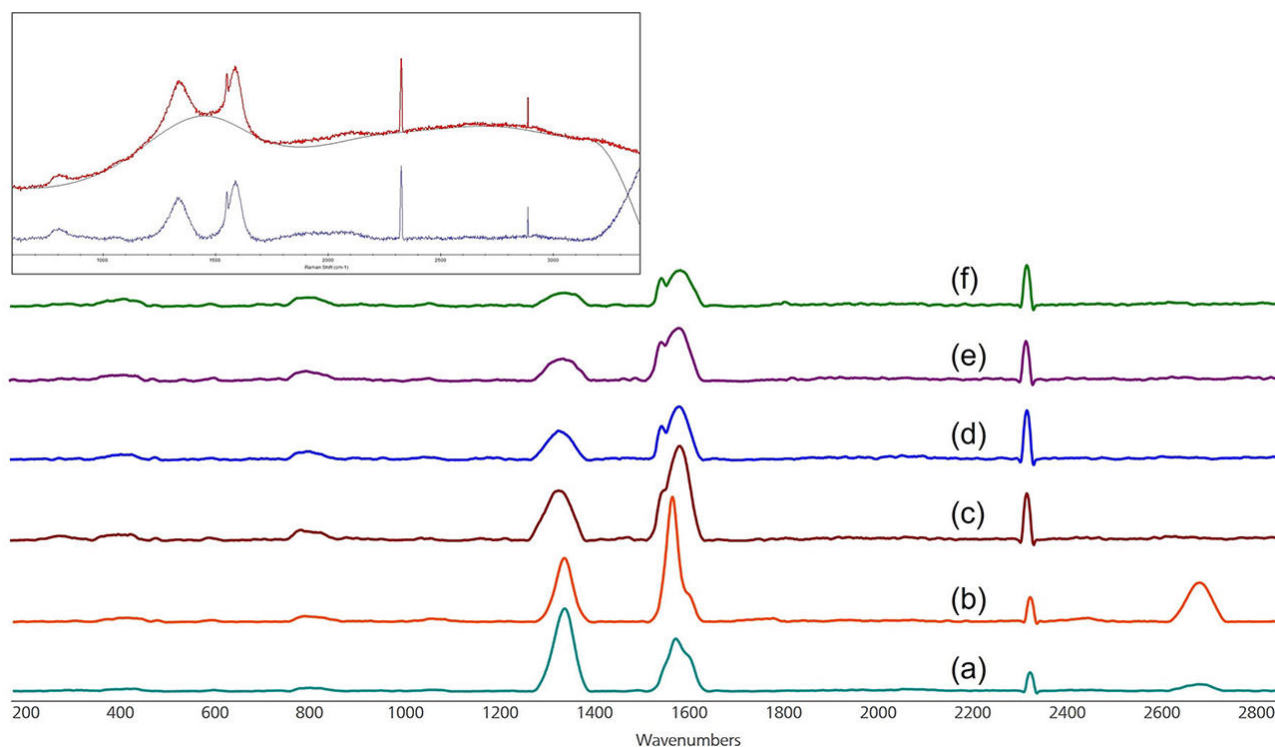
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**Figure 3.** Raman spectra of carbon nanofibers (a,b) and carbon black powders (c–f). The insert shows an example of the baseline correction that was applied to all data. All spectra are manually offset for clarification.

## 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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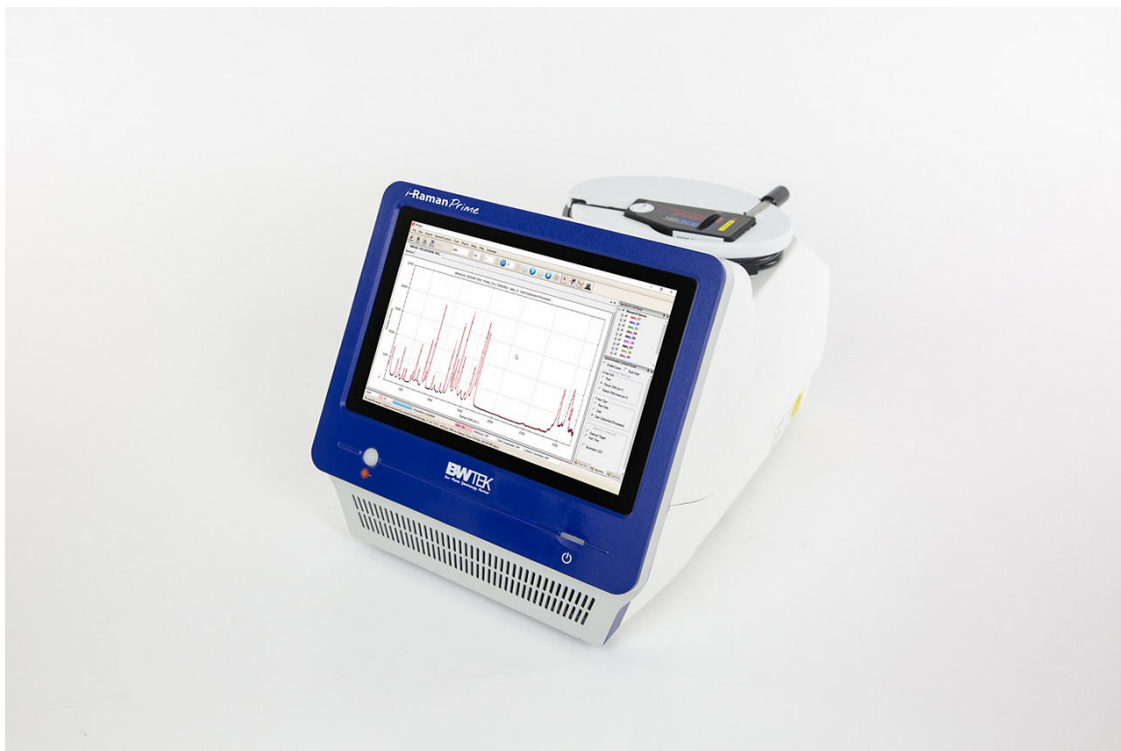
## REFERENCES

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
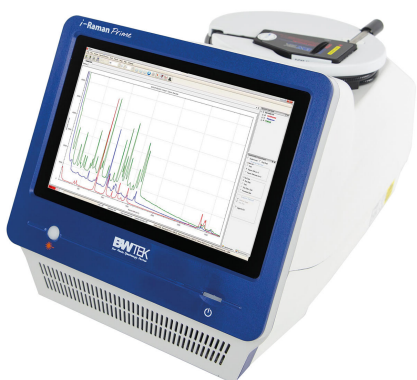


## i-Raman Prime 532H

 i-Raman® Prime 532H 是一高物料通量、低噪声且完整集成的拉曼系,内置平板和一个光采探。便携式拉曼光有高量子效率、TE 深度冷却功能 (-25°C)、高范的 CCD 列器,可研究的拉曼分析,包括定量和定。由于具有高的物料通量,拉曼光提供了佳的信噪比,并借此可以量更快速的程,并且即使是最弱的拉曼信号也可以到微的品差。

除了其移式形式外, i-Raman Prime 532H 具有光范和高分辨率的独特合,并而可以行 150 cm$^{-1}$ 至 3400 cm$^{-1}$ 的量。 i-Raman Prime 可使用蓄池行,并而方便。因此,无什地方都可以行研究的高精度以及高量和高定量的高量拉曼分析。系化,可与我的 STRaman® 技搭配使用,可用于通非透明包装行分析。
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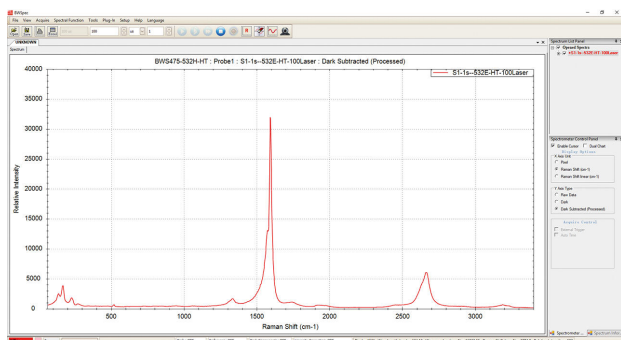


## BWSpec

BWSpec® 是一款 B&W 的常光件,用于器控制和数据采集,包括波峰分析和。BWSpec 是所有 B&W Tek 便携式拉曼系和光品随附的一款操作件。其用功能广泛,只需点一个按即可行的量和算。其支持多重数据格式并能提供化量参数,比如分和激光出功率控制。除了数据采集和数据理外,它提供自暗去除、光平滑、基校正以及峰和分析。

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