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# Graphene Raman Analyzer: Carbon Nanomaterials Characterization
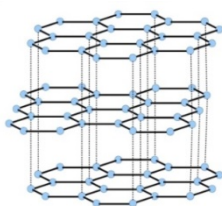
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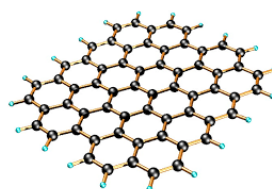
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## Introduction

Carbon nanomaterials constitute a variety of carbon allotropes including graphene, graphene oxide, carbon nanotubes, and carbon nanofibers, each exhibiting unique properties in electrical conductivity, thermal conductivity and mechanical strengths thanks to the distinctive structures of each allotrope. Graphene is a 2D material formed from a hexagonal lattice of carbon atoms. Graphite is made up of individual stacked layers of graphene. Graphene's strength, superconductivity and excellent heat conductivity makes it a very attractive material as a conductor in memory chips and in batteries [1]. Graphene oxide, an alternative form of graphene, can be used to desalinate water and remove radioactive isotopes due to its permissibility of water [2].  Carbon nanotubes, which are tubes with walls formed from graphene sheets, have attracted interest from industry to potentially generate high surface area catalysts in fuel cells with the addition of different functional groups [3]. Carbon nanotubes can either be single-walled (SWNT) or multi-walled (MWNT). Carbon nanofiber, which is a mix of carbon black and carbon nanotubes, has found applications in construction materials thanks to its flexibility and durability [4].
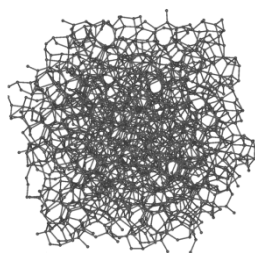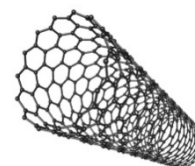


Carbon black (amorphous)  Graphite  Monolayer graphene  Carbon nanotube

Largely heralded as a "wonder material" since its discovery in 2004, graphene has now entered the era of industrial manufacturing. Although the 2016 Deloitte global prediction report on the graphene industry predicted the value of the global graphene market to be only in the low tens of millions of dollars [5], the current research and development spending on graphene is likely to be in the hundreds of millions of dollars. It may be decades before the potential of these carbon nanomaterials is fully realized, but in the medium term graphene may be incorporated into products worth billions of dollars.

Graphene can be made through various processes [6]: 1) mechanical exfoliation, which is usually done on a smaller scale; 2) CVD (chemical vapor deposition), which is performed on a relatively larger scale but at a high cost and with expensive equipment; and 3) exfoliation and reduction of graphene oxide, which is synthesized through the oxidation of graphite powder on a larger scale but can result in extensive defects. For large-scale graphene manufacturing, one important question remains: how to easily and rapidly characterize the quality of graphene and other carbon nanomaterials to effectively monitor and control the production process.

Raman spectroscopy has been used extensively by carbon nanomaterials research communities in recent years because of its ability to characterize materials from molecular vibrations. The Raman spectra of carbon nanomaterials are typically characterized by three major bands: the G-band, the D-band, and the 2D-band (also referred to as the G'-band). Though simple, the spectra of these nanomaterials are rich in information about their quality and their micro-structures as revealed by the peak positions, peak shapes, and peak intensities. The G-band appears around $1582 cm^{-1}$ and represents the graphene in-plane $sp^2$ vibrational mode; it is an indication of the crystallinity of the material. The dispersion of the G-band can be observed in disordered graphene materials, and the dispersion is proportional to the degree of disorder. The D-band at around $1350 cm^{-1}$ is attributed to the structural disorder near the edge of the microcrystalline structure that decreases the symmetry of the structure. The Raman peak intensity ratio of these two bands, $I_D/I_G$, can be used to characterize the degree of disorder of the materials [7]. The 2D-band appears around $2700 cm^{-1}$ depending on the laser excitation wavelength and is related to the number of graphene layers [3].
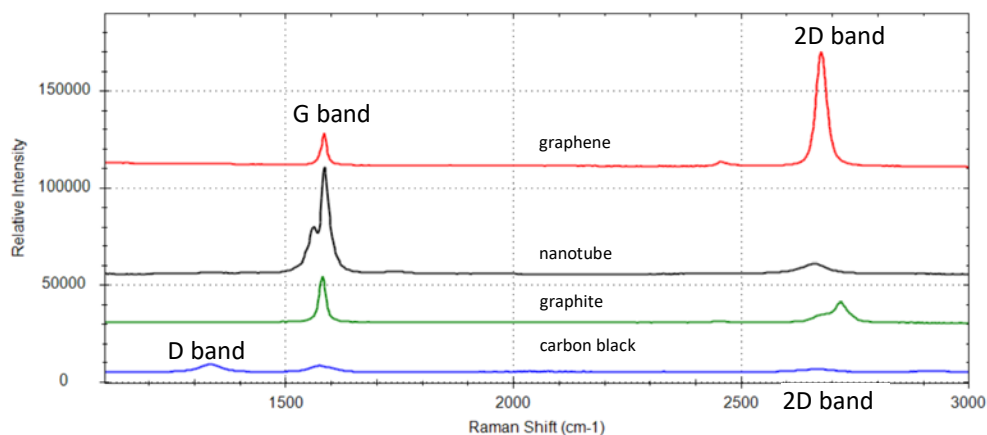


Fig. 1 Raman spectrum of graphene (red), carbon nanotubes (black), graphite (green), and carbon black (blue)

The Raman spectra of monolayer graphene (red trace), carbon nanotubes (black trace), single crystal graphite (green trace), and carbon black powder (blue trace) are shown in Figure 1. Graphene is characterized by the sharp, symmetric single peak of 2D-band. The graphite spectrum displays a high amount of order and thus crystallinity characterized by its prominent G-band and the absence of a D-band. Since graphite is composed of many layers of monolayer graphene, the 2D-band observed in the graphite spectrum is much broader and asymmetric than the graphene 2D-band, indicating multiple components from several phonon modes. Carbon nanotubes display unique features of G-band. Due to the confinement and curvature of graphene layers in forming nanotubes, the G-band becomes asymmetric for MWNT and more likely splits into two bands, the G+ and the G-band for SWNT [7]. The spectrum of carbon black, which has the lowest amount of crystallinity, displays a strong D band and broad G band, with a high $I_D/I_G$ ratio, indicating a disordered structure.

Raman spectroscopy provides rich information about the characteristics of carbon black, graphite, graphene, and other carbon nanomaterials. Although confocal Raman microscopy can provide high-resolution characterization of carbon nanomaterials, the high cost of this instrumentation coupled with the complexity in operation and data interpretation is inadequate for monitoring in a large-scale manufacturing setting, where simple and rapid analytical tools are required. In this study, a high-throughput portable Raman analyzer is used to characterize three types of materials: graphene powder coated sheets, carbon nanofibers, and carbon black. This quick analysis can be applied as an at-line or on-line technique for graphene and other carbon nanomaterials for materials characterization, product quality control, and process monitoring.

**Experimental**

The high-throughput i-Raman® Pro HT from B&W Tek (Figure 2) with a laser excitation of 532 nm via a fiber-optic sampling probe was used for measurements of all samples. The i-Raman Pro HT utilizes a high throughput Raman spectrometer with a back-thinned CCD TE-cooled to -25°C. For materials in powdered forms, no microscope is needed. A probe holder with an adjustable *xyz* stage was used to support the fiber-optic probe over an aluminum pan containing a given carbon sample. The *z*-focus was used to optimize the working distance from the probe to the sample.
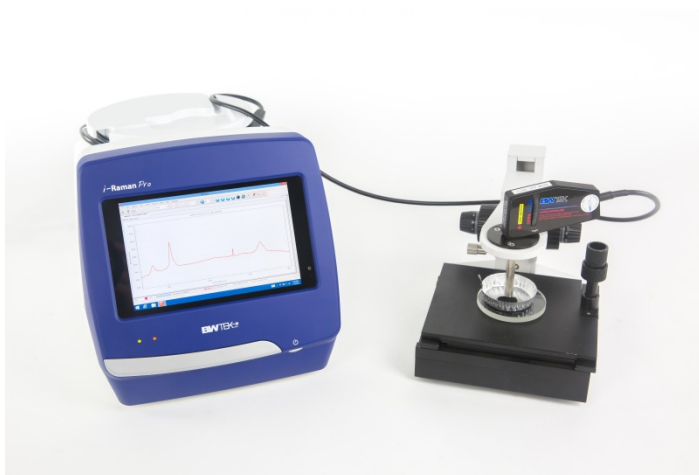
Fig. 2 i-Raman Pro HT setup for analysis of carbon nanomaterials (enclosure not included)

BWSpec software was used for data collection, spectral processing, and programming the calculation of peak intensities and ratios. BWSpec allows the user to configure analysis parameters and conduct on-line experiments in real-time. Off-line batch processing is also possible. The software allows for up to six variables to be calculated and monitored with results displayed in a control chart and tabulated simultaneously.

Three types of carbon nanomaterials are analyzed using the i-Raman Pro HT: sheets coated with graphene powders, carbon nanofibers, and carbon black powders. For all sheets coated with graphene powders, laser power of 35 mW with integration time of 60s was used to acquire Raman spectra. No spectral averaging was applied. For carbon nanofiber and carbon black powder samples, an integration time of 90s was used with a laser power of ~21 mW. Three spectra were collected for each sample. For all collected spectra, an adaptive iteratively reweighted Penalized Least Squares (airPLS) background correction was used to remove any fluorescent background present in the spectra. A Savitzky-Golay smoothing algorithm with a window size of 2 was also applied to all spectra.

**Test Results**

Graphene powders

Six sheets coated with graphene powders were tested. Figure 3 shows the manually offset representative spectra for each graphene sample. The D-band, G-band, and 2D-band can be observed from all sample spectra. Graphene #6 presents the most intense D-band and the weakest 2D-band, as well as a prominent D' band at 1620 cm$^{-1}$ that is consistent with defected graphene [8]. There is also a slight shift in the position of the G-band. This information indicates

that graphene #6 has the highest disorder and thus the least graphene characteristics among all the samples.

BWSpec software was programmed to automatically calculate the $I_D/I_G$ value for each measurement. Table 1 presents the calculated peak intensities and intensity ratios for the D- and G-bands.
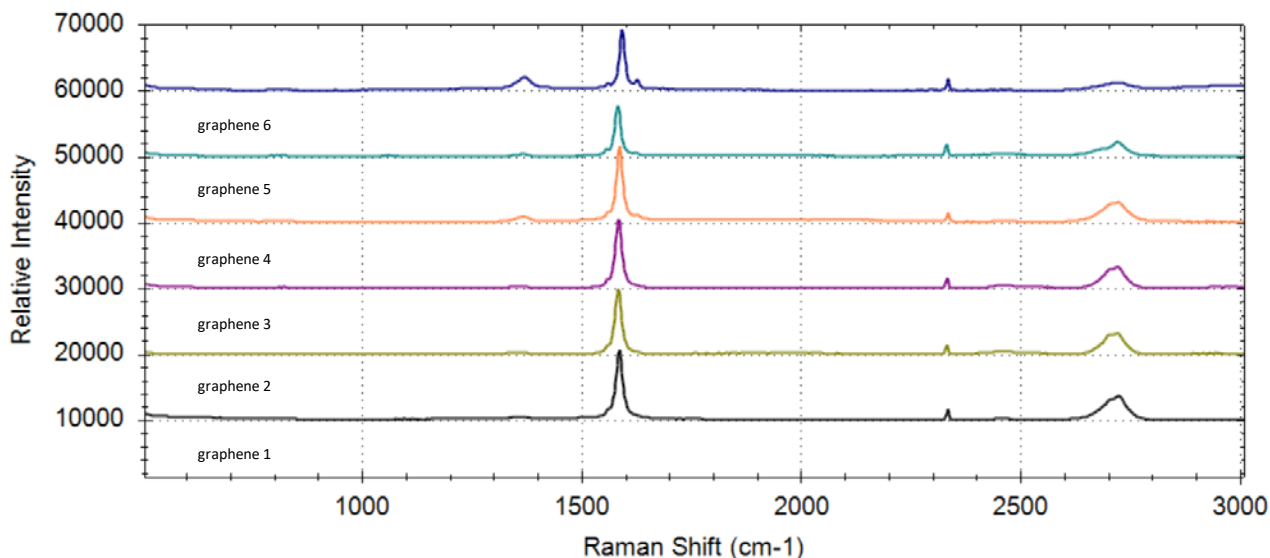


Fig. 3 Raman spectra of six graphene samples

Table 1. Calculation of the D-band height, G-band height, and $I_D/I_G$ for all graphene samples

| Sample | $I_D$ | $I_G$ | $I_D/I_G$ |
|--------|-------|-------|-----------|
| 1 | 216.2524 | 2851.3339 | 0.0758 |
| 2 | 184.2049 | 2898.9823 | 0.0635 |
| 3 | 210.1374 | 3067.5027 | 0.0685 |
| 4 | 449.2745 | 2987.0646 | 0.1504 |
| 5 | 188.0537 | 2101.317 | 0.0895 |
| 6 | 957.5563 | 2052.6019 | 0.4665 |

G-band dispersion is observed among the graphene samples with graphene #4 and graphene #5 showing noticeable difference from each other (Figure 4) with calculated G-band full width at half maximum (FWHM) for sample #4 and #5 displayed. As presented in Figure 5, all of the 2D-bands from the samples are asymmetric, which is characteristic of graphene powder. Some significant differences in the shape and intensity among all 2D-bands can be seen. Graphene #5 has the most defined 2D-band. This further indicates that graphene #5, similarly to samples #1, #2, and #3, has a high degree of crystallinity, less disorder and fewer layers of graphene.
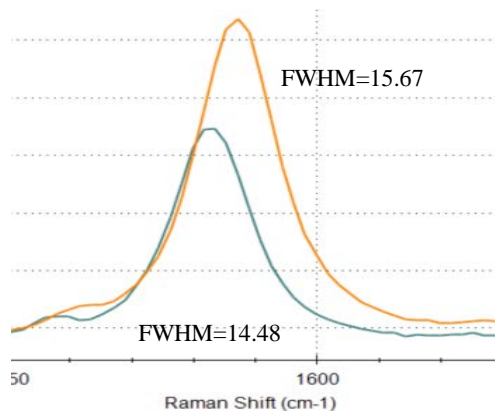
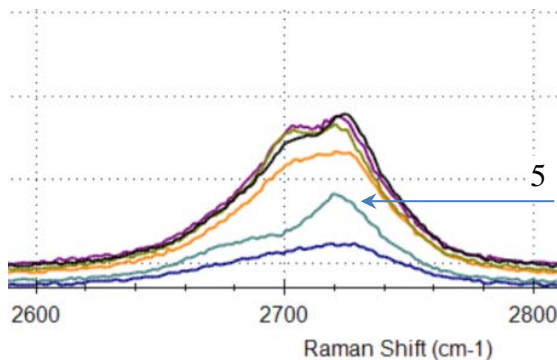Fig. 4 G-band for graphene #4 (orange) and #5 (green) with labeled FWHMs



Fig. 5 2D band for graphene samples #1 to #6

## Carbon nanofibers and carbon black

Two carbon nanofiber samples and four carbon black samples were tested. Three spectra were collected for each sample. Figure 6 shows the manually offset representative spectra for each sample. The four carbon black samples display typical carbon black Raman signatures that contain D- and G-bands but no 2D-band. The two carbon nanofiber samples show prominent D-bands, indicating a high level of disorder. The G-bands in the carbon nanofiber spectra also exhibit some asymmetry. The asymmetry could come from the nanotubes, with the slight splitting of the G-band induced by curvature of graphene layers when forming the nanotubes.
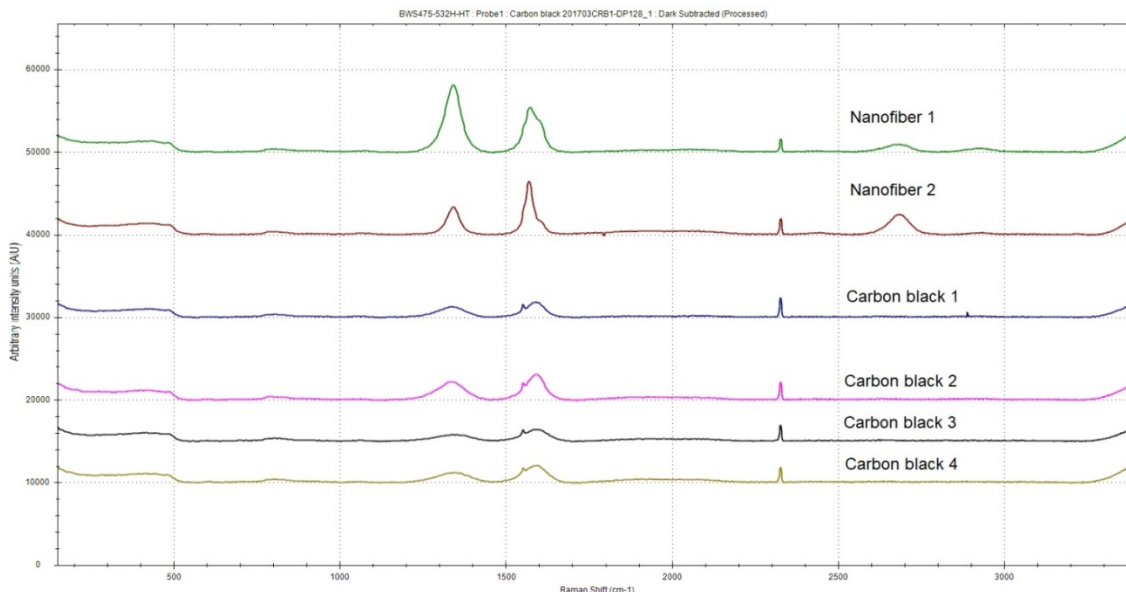
BWSpec software was used to automatically calculate the $I_D/I_G$ values as spectra were collected. Table 3 presents the calculated $I_D/I_G$ peak intensity ratios measured for the four carbon black samples and two carbon nanofiber samples. The carbon nanofiber sample #2 has the highest level of order of all samples with an average $I_D/I_G$ of 0.4706, while the carbon nanofiber sample #1 has an especially high level of disorder with an average $I_D/I_G$ of 1.3654.

Table 3 Average calculated peak intensity ratios for D-band and G-band

| Carbon type | Average peak ratio (n=3) |
|---|---|
| Carbon black 1 | 0.7667 |
| Carbon black 2 | 0.7294 |
| Carbon black 3 | 0.5557 |
| Carbon black 4 | 0.5745 |
| Carbon nanofiber 1 | 1.3654 |
| Carbon nanofiber 2 | 0.4706 |

Fig. 6 Raman spectrum of two carbon nanofiber samples and four carbon black samples

It is worth noting that the Raman spectra for two carbon black samples (Figure 7) reveal two peaks at ~ 213cm$^{-1}$ and 280cm$^{-1}$ that are consistent with $Fe_2O_3$ hematite. It is a known fact that there may be up to 10% of residual iron content in the nanofiber samples from the manufacturing process. The two hematite bands distinctively confirm that presence of iron oxide.
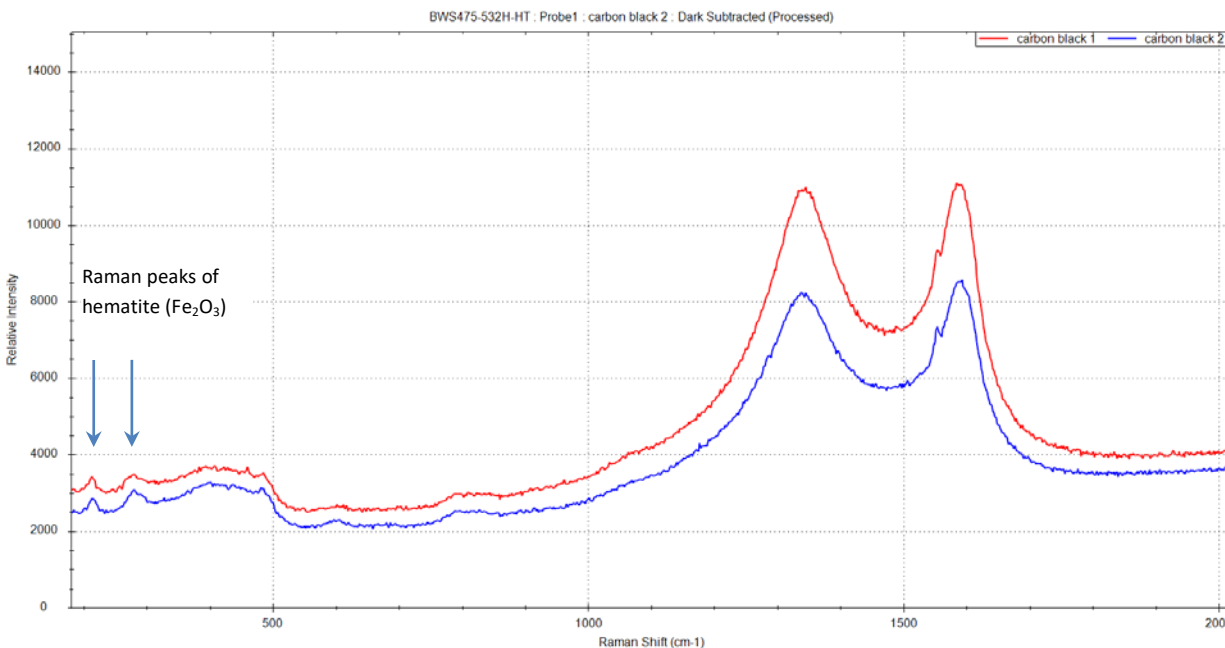


Fig. 7 Raman peaks of hematite $Fe_2O_3$

## Conclusions

Although simple, a Raman spectrum of a carbon nanomaterial can provide a vast amount of information to characterize materials including carbon black, graphite, carbon nanotubes, and graphene. B&W Tek's i-Raman Pro HT is capable of quickly characterizing carbon nanomaterials, revealing critical information regarding material qualities such as sample crystallinity and level of disorder. BWSpec acquisition software can be programed to automatically calculate various parameters such as D- and G-band intensity ratios and band FWHM. Graphene manufacturers can easily use the analysis to obtain at-line or on-line measurements for material characterization, product quality control, and process monitoring.

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