Carbon Black At-line Characterization

Using a Portable Raman Spectrometer

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Abstract

Carbon black is a form of amorphous carbon. It is mainly used as reinforcement filler in automobile tires and other rubber products, but is also used in pigments, paint, and carbon paper. Raman spectroscopy is a very effective analytical technology to characterize carbon materials. The Raman bands associated with different carbon bonds reveal details of the structure on the molecular level. Most of the research using Raman technology has been applied to carbon nanotubes and graphene. The fast characterization of carbon black material using Raman spectroscopy is discussed here to demonstrate that Raman technology is well suited for carbon black material characterization. A portable Raman spectrometer is a very effective analytical tool for carbon black material manufacturing at-line process control and monitoring.

Introduction

Due to the highly selective, unique chemical signatures contained in Raman spectra and the fact that the intensity of Raman peaks is proportional to the related compound concentration, Raman technology has been used as a molecular fingerprint to analyze molecular structures, to identify specific molecules, and to predict the chemical concentrations in mixtures. With Raman technology advancing into the development of portable Raman systems with lab grade performance, and also due to the non-destructive nature and the fact that no sample preparation is required for testing, Raman spectroscopy has become a go-to method of analysis in practical, real world applications. For example, in raw material verification, quick identification of unknown chemical compounds, mixture identification and quantitative analysis in mixtures, Raman has been widely adopted by pharmaceuticals, chemical companies, and safety and security agents throughout the world. In addition, the peak intensity ratio between two Raman signature peaks can also provide useful information on material crystallinity, phase transition, and material structure disorder.

In this article, portable Raman for at-line characterization of carbon black is explored. Because of the distinctive information contained in the peak ratio between the D-band and G-band of sp^2 carbon material, Raman spectroscopic analysis can be an effective test to characterize carbon black material. The portable Raman spectrometer used in this study showcases the versatility of Raman spectroscopy and the potential impact that the new generation portable Raman spectrometers will have to various industries.

Carbon Black Materials

Carbon black material is graphite in an amorphous structure, with a lower level of crystallinity than graphite. It is mainly used as reinforcing filler in automobile tires and other rubber products, and is also used in pigments, paint, and carbon paper. Due to the complexity of the material structure and lack of definitive standard test methods, material characterization is rather limited to conventional tests[1], including: surface area, particle size estimated from the surface area values, iodine adsorption numbers for evaluation of carbon black grades, and dibutyl phthalate (DBP) absorption numbers to determine the relative amount of oil that carbon blacks can absorb. While there are technologies such as X-ray diffraction analysis or high performance imaging analysis that can depict the carbon black material structure on the atomic level, none of the methods allow for the quick and convenient on-line or at-line real-time testing on the molecular level that may help evaluate, control and monitor the carbon black manufacturing process.

The carbon microstructure is highly Raman active, making Raman uniquely suited for analysis of carbon materials in different crystal structures. Graphite contains hexagonal planes of carbon atoms, with four carbon atoms in one unit cell. The different planes are connected by translations or rotations around the symmetry axis[2]. For the single crystal graphite symmetric group D_{6h}^4, one of the vibrational modes E_{2g} is strongly Raman active and is associated with a Raman peak at 1582cm^{-1} (G-band)[3]. As a result, graphite with highly single crystallinity, under the name of HOPG (Highly Ordered Pyrolytic Graphite), only displays a Raman peak at 1582cm^{-1}. Figure 1 shows the graphite structure of the E_{2g} mode that is associated with the G-band. For carbon black material with amorphous microcrystalline structures, another peak around 1350 cm^{-1} (D-band) will also appear. It has been concluded that the peak at 1350cm^{-1} is attributed to the structure disorder near the edge of the microcrystalline that destructs the structure of the symmetry[3]. Therefore, the Raman peak intensity ratio of I_D/I_G can be used to characterize the degree of disorder of the graphite materials. Researchers also believe that the I_D/I_G is inversely proportional to the grain size of the carbon black materials for grain sizes larger than 2nm[4]. Figure 2 displays Raman spectra of three different carbon black samples with the noted D-band and G-band, collected using the portable Raman spectrometer i-Raman Plus with 532nm laser excitation.

Experiment

Commercially available carbon black materials were characterized by Raman spectroscopy using B&W Tek's portable Raman spectrometer, i-Raman Plus® with a 532 nm laser excitation and spectral resolution at 4.5 cm^{-1}. A portable video microscope sampling system is coupled with the portable i-Raman Plus system to facilitate accurate laser focus on the sample surface. Figure 3 shows a picture of the experimental setup. The Raman spectra were collected at room temperature with an integration time of 120s using laser power around 40mW. Because

of the low efficiency of the Raman phenomenon (10^{-8}), it is important that the readout noise and dark noise for the CCD detector in a Raman spectrometer remains very low relative to the Raman signal. A back-thinned CCD detector with TE-cooling to -2°C is used in the i-Raman Plus. Compared to a conventional front illuminated CCD with quantum efficiency around 50%, the back-thinned CCD quantum efficiency can reach up to 90% with photons entering from the back side of the CCD where the Si substrate is etched thin to enhance the light reaching the CCD active area. This can largely increase the quantum efficiency by reducing the photon loss. The TE-cooling of the CCD device effectively reduces the dark noise: the dark noise halves for each 7°C decrease in device temperature. The cooled detector allows for long integration time, such as the 120 seconds in the experiments in this study. This greatly increases the detection limit and makes some of the low-light level applications possible.

The software BWSpec™ was used for data analysis, which includes baseline correction and peak analysis. Any fluorescence that may accompany the Raman signal can be removed by the baseline correction function in BWSpec, which is based on a novel algorithm adaptive iteratively reweighted Penalized Least Squares (airPLS). With the airPLS algorithm, weights of sum squares errors (SSE) are iteratively changed between the fitted baseline and original signals, while the weights of the SSE are adapted using the difference between the previously fitted baseline and the original signals[5]. Figure 4 demonstrates the Raman spectrum of carbon black before and after the airPLS baseline correction. After the baseline correction, the Raman peak intensities can be obtained easily using the peak analysis function of the software. The Raman peak intensity ratio of the D-band and G-band can then be calculated.

Figure 5 shows the Raman spectra of three different carbon black materials after baseline correction. The D-band and G-band peak positions, peak intensities, and peak ratio I_D/I_G of three samples are calculated and displayed in Table 1. One feature of the D-band that makes it more interesting is that the D-band position is not independent of the excitation laser wavelength. It was reported[6] that the D-band peak position is shifted from 1360cm^{-1} to 1330cm^{-1} when the laser excitation changed from 488nm to 647nm. As demonstrated in the experiment, the D-band peak position is around 1337cm^{-1} when using 532nm laser excitation. For sample C1 and C2, the I_D/I_G ratios are less than one, indicating that these carbon black materials have some degree of disorder, which is in the typical range of graphite rod (C1)[3] and graphite powder (C2)[3]. For sample C3, the I_D/I_G ratio is larger than one, which indicates that the sample has a higher degree of disorder.

Sample	D (cm^{-1})	G (cm^{-1})	I_D	I_G	Peak Ratio I_D/I_G
C1	1337	1586	909.4	1120.5	0.81
C2	1337	1581	2763.1	2828.1	0.98
C3	1336	1574	4022.5	3263.2	1.23

Table 1. Peak info of the D-band and G-band for three carbon black samples with 532nm laser excitation

Conclusions

The high sensitivity of the Raman spectrometer provides quality spectrum of carbon black materials with distinctive D-bands and G-bands. Correlations between the Raman spectra and the structure can be established. The G-band represents the level of order of graphite in its single crystalline form. The presence of a D-band is related to the level of disorder of the crystal structure with reduced symmetry of the sp^2 carbon. The ratio of I_D/I_G can be used to characterize carbon black material in several aspects including: 1) the degree of disorder of the carbon black; 2) an estimation of the grain size of the carbon black materials; and 3) batch uniformity when multiple measurements are taken at different locations of the materials. The fact that portable Raman spectrometers can provide quality spectrum makes it possible to perform at-line or on-line analysis of carbon black materials. This will benefit carbon black manufacturing for process control and process monitoring. Compared to large bench-top lab-grade Raman spectrometers which cannot be easily placed on-line or at-line for real time analysis, the new generation portable Raman spectrometers have demonstrated large potential in industrial applications and will play a more important role in the near future.

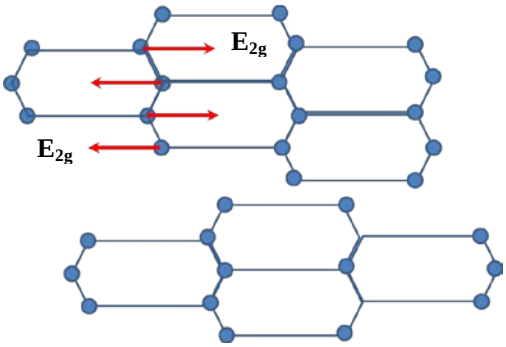

Figure 1. E_{2g} vibrational mode of carbon atoms in one graphite layer

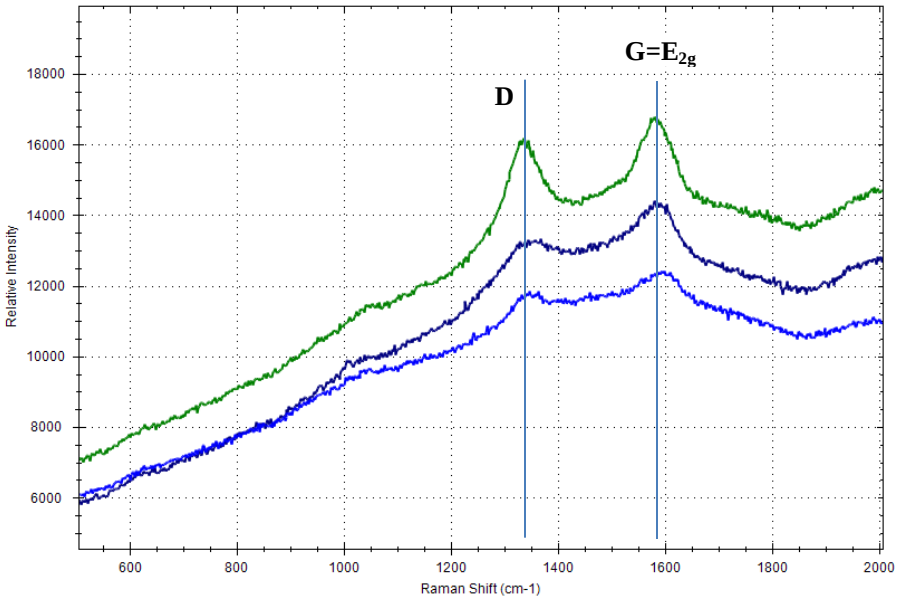

Figure 2. Raman spectra of carbon black materials with D-band and G-band

Figure 3. Experiment setup

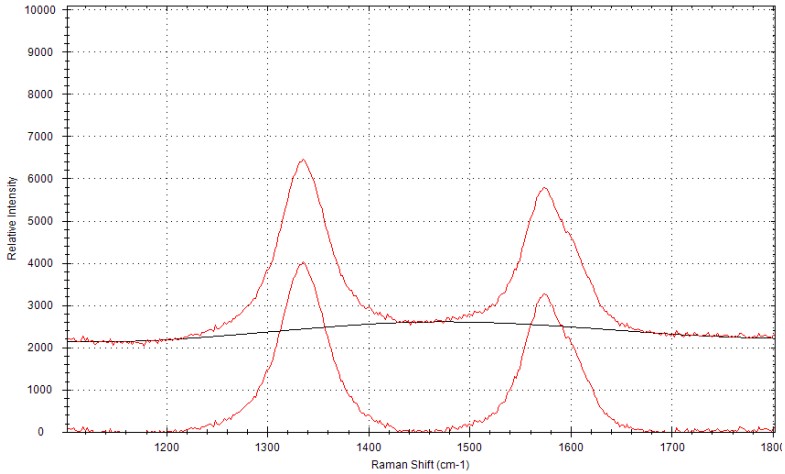

Figure 4. Raman spectrum of carbon black before and after the baseline correction

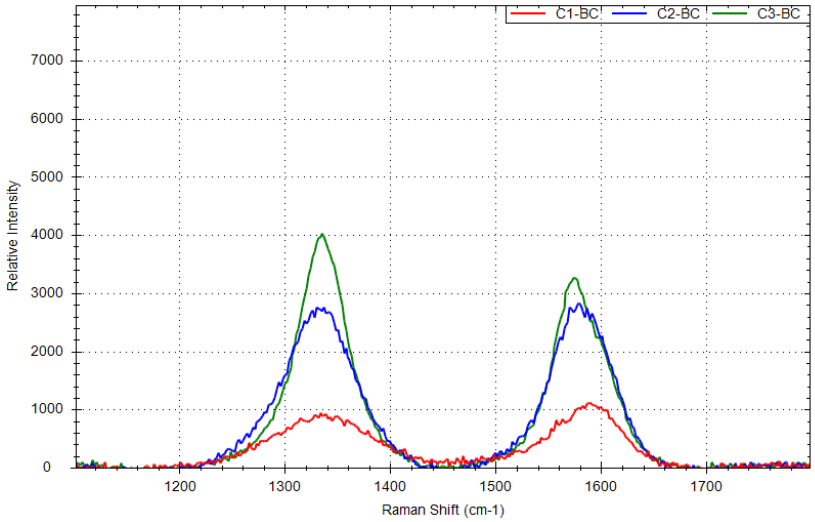

Figure 5. Raman spectra of carbon black samples after the baseline correction with different I_D/I_G: red is for C1, blue is for C2, green is for C3.

References

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Additional Resources

i-Raman Plus datasheet
BAC151 Raman Video Microscope datasheet
BWSpec datasheet

If you have any questions about the application or would like to know how Raman would work for your application, please contact us at appnote@bwtek.com or call us at +1 (855) 297-2626 to speak with an expert.

