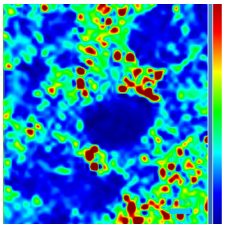
HORIBA

Raman

Optimizing Carbon Material Analysis with Raman Spectroscopy



Application Note

Carbon
RA93

H. Elazri[1], C. Eypert[1], Z. Pengyu[2]

[1]HORIBA FRANCE SAS, Palaiseau, France, [2]HORIBA Trading Co.,Ltd., Beijing, China

Abstract: The characterization of carbon materials is crucial in various industries, particularly for ensuring the quality of lithium-ion batteries (LiBs). This application note explores the background and challenges associated with traditional analysis methods, and presents HORIBA's advanced solutions, including ParticleFinder™ for studying carbon particles morphology and QCarbon for analyzing the D/G intensity ratio using Raman mapping. We showcase the capabilities of our integrated approach by characterizing an unknown sample of carbon powder, illustrating how HORIBA's innovative technology delivers precise and efficient characterization of the sample.

Keywords: Raman microscopy, Carbon materials, Particle size, Quality control

Introduction

Carbon materials such as graphene, carbon black (CB), and carbon nanotubes (CNTs) are integral to numerous applications due to their exceptional properties, including high electrical conductivity, mechanical strength, and thermal stability. These attributes make them valuable in fields ranging from electronics and energy storage to composite materials and nanotechnology. [1]

Given the structural diversity and presence of various defects and functional groups in carbon materials, precise characterization is crucial for optimizing their performance for high energy or power density. Raman spectroscopy has emerged as a powerful tool for analyzing carbon materials. This non-destructive technique provides detailed information about the structural and electronic properties of carbon-based materials. Raman spectroscopy is adept at identifying defects, disorder, and the degree of crystallinity. It can distinguish between different forms of carbon, such as graphite, amorphous carbon, and various types of graphene and CNTs [2].

In the context of lithium-ion batteries, Raman spectroscopy is invaluable for studying electrode materials, providing insights into the state of charge, structural changes during cycling, and degradation mechanisms. By analyzing Raman spectra, researchers can monitor the quality and consistency of carbon materials, ensuring they meet the stringent requirements for high-performance energy storage systems.

However, the complexity and variability of carbon materials present significant challenges in meeting the demands of modern industries, especially for lithium-ion batteries (LiBs). Advanced analytical methods, such as transitioning from 2-peak to 4-5 peak fitting, are necessary to capture detailed characteristics of emerging carbon materials. Particle size distribution and morphology critically influence electrode performance, but traditional methods often fail to characterize these properties accurately, leading to inconsistent quality. Existing quality control processes are labor-intensive and inefficient, reducing productivity and reliability. Ensuring precise measurements is difficult due to the heterogeneity of carbon materials, requiring accurate baseline correction, signal-to-noise ratio management, and reliable peak fitting, all of which demand specialized expertise.

HORIBA Solution

HORIBA addresses these challenges with state-of-the-art Raman microscopy solutions, enabling precise and efficient analysis of carbon materials. Two key tools in HORIBA's portfolio are ParticleFinder™ and QCarbon, each offering unique capabilities to enhance carbon material characterization. ParticleFinder™ facilitates the study of carbon particle morphology, providing critical insights into particle size and shape, while QCarbon specializes

in analyzing the D/G intensity ratio on Raman mapping, delivering detailed information about the structural properties of carbon materials.

ParticleFinder™ + XD-100 Particle Disperser

HORIBA offers a comprehensive solution for carbon particles analysis, featuring both the ParticleFinder™ and the XD-100 Particle Disperser.

The ParticleFinder™ is an advanced tool designed for automated location, characterization, and Raman analysis of particles. It simplifies the workflow by quickly locating hundreds or thousands of particles on a video image, analyzing their size and shape descriptors, and then performing chemical characterization using Raman spectroscopy. Its features include automated detection, size and shape analysis, and chemical characterization, all integrated into a streamlined workflow with the LabSpec 6 software.

In conjunction with this, the XD-100 Particle Disperser ensures precise and efficient sample preparation by uniformly dispersing carbon materials without damaging the particles, enhancing the accuracy of subsequent analyses.

Figure 1: picture of the XD-100 Particle Disperser

We used this combined solution to characterize the particles of the unknown powder. We dispersed the powder on a glass microscope slide, then performed ParticleFinder analysis with the XploRA PLUS Raman microscope. The software automatically locates particles directly from the optical image, as shown on the picture below. A Raman acquisition is then performed on each particle to identify its chemical nature. The full measurement was completed in just 30 minutes, demonstrating the high throughput of this solution and its capability to quickly process large volumes of data.

The software identified three types of carbon as seen in the graph below. Spectrum A, with strong peaks at 1350 cm^{-1} and 1580 cm^{-1}, corresponds to graphite or graphene, characterized by its highly ordered structure. Spectrum B, showing a pronounced peak around 1600 cm^{-1}, is indicative of graphene oxide, which has a more disordered structure compared to pure graphene, due to the higher D/G ratio. Spectrum C, with a D/G ratio of 0.9, likely represents an intermediate state of carbon between graphite and graphene oxide, potentially a partially oxidized or reduced form of graphene.

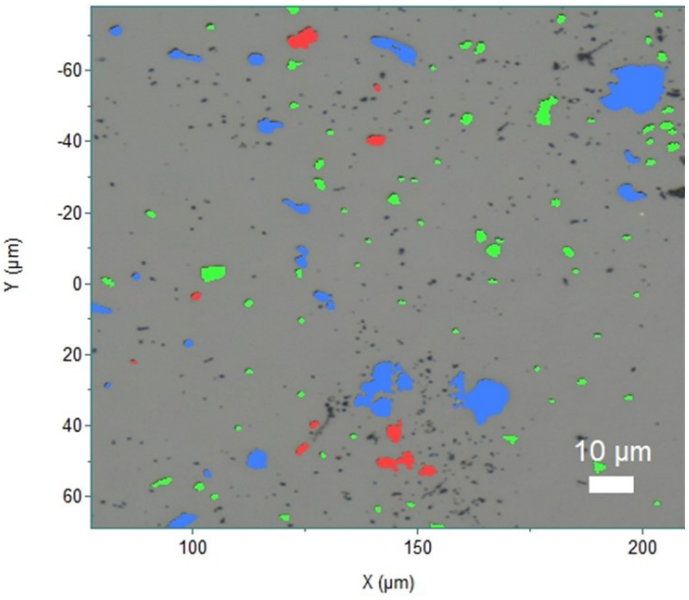


Figure 2: Optical image of the glass slide where ParticleFinder detected the particles and colored them with the color of the associated spectrum

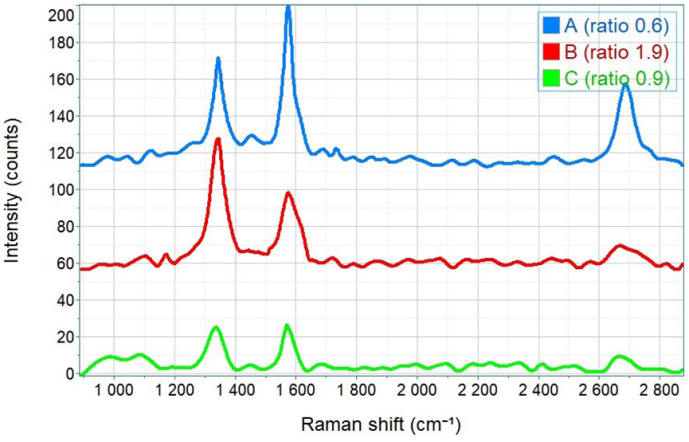


Figure 3: Raman spectra of the three main components of the carbon powder

The software also provides detailed morphological analysis, including statistical summaries and histograms for parameters such as area, perimeter, and circularity. The graph below represents the histogram of diameters for the three types of carbon. It shows that type C (intermediate state carbon) consists mainly of smaller particles (<5 µm), type B (graphene oxide) has a moderate distribution across the size ranges, and type A (graphite/graphene) includes a broader range of particle sizes, including larger particles (>10 µm). This distribution suggests that higher structural order corresponds to larger particle sizes, while increased disorder or oxidation results in smaller particle sizes.

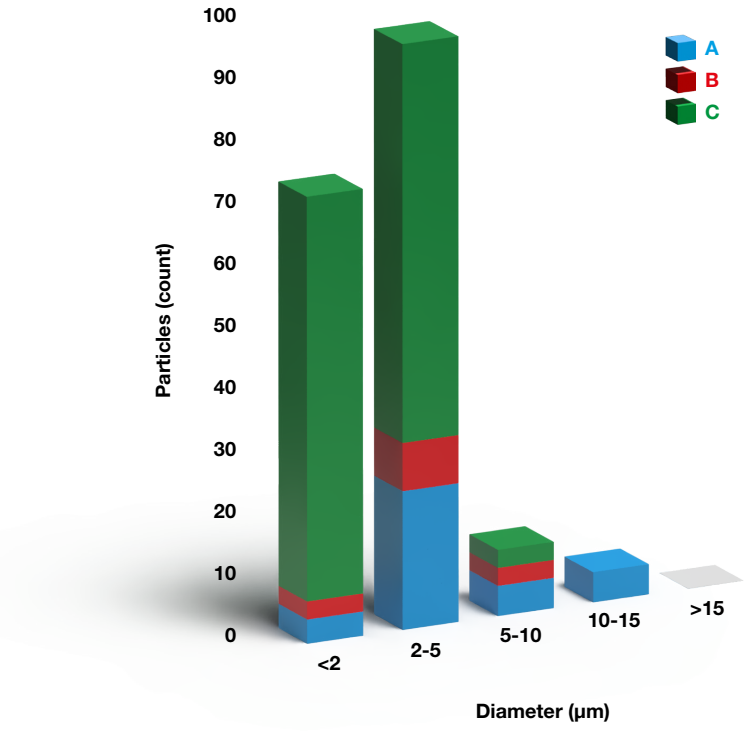


Figure 4: Histogram of diameters of the carbon particles, the colors in the histogram correspond to the colors of the reference spectra

Using HORIBA's ParticleFinder™, we chemically and morphologically characterized the unknown powder, identifying three types of carbon: graphite/graphene, graphene oxide, and an intermediate state. We also obtained detailed statistics about the morphology of these particles, such as their diameter distribution, linking higher structural order with larger particle sizes and increased disorder or oxidation with smaller sizes.

QCarbon

QCarbon is designed to optimize the analysis of carbon materials through advanced Raman spectroscopy techniques. This tool specifically targets the analysis of the D/G intensity ratio on Raman mapping, providing detailed insights into the structural properties of various carbon materials.

Enhanced Analysis Methods

In order to quantitatively analyze the Raman spectra for the carbon materials, a curve fitting method which is universally applicable to a wide range of carbon types is necessary. [3] QCarbon introduces a sophisticated 5-peak fitting technique for more accurate characterization of carbon materials. This method utilizes a combination of Gaussian and Lorentzian fits to accommodate different peak shapes, crucial for analyzing complex carbon structures. [4]

The five key peaks include:

- G band (~1580 cm^{-1}): Representing the ideal graphite lattice.
- D1 band (~1350 cm^{-1}): Indicating disorder in the graphite lattice.
- D2 band (~1620 cm^{-1}): Weakly present, representing additional disorder.
- D3 band (~1500 cm^{-1}): Associated with amorphous carbon.
- D4 band (~1200 cm^{-1}): Further indicative of disorder in the graphite lattice.

Automated Reporting

QCarbon streamlines the entire analysis process with its one-click report generation feature. The automated workflow includes:

- Data Acquisition and Processing: Automated steps for range cutting, de-spiking, smoothing, and baseline correction ensure high-quality data.
- Peak Analysis: The system identifies and fits peaks, calculating their amplitudes, areas, and widths, and generating statistical data such as mean values and standard deviations.
- Report Generation: Processed data is compiled into customizable reports, providing a comprehensive overview of analysis results.

This automation significantly reduces the time required for QC processes, enabling faster decision-making and improved operational efficiency.

Methods and Correctness

To ensure accuracy and reliability, QCarbon employs rigorous pre-processing methods like despiking and baseline correction. The fitting parameters are carefully adjusted to match the specific characteristics of different carbon materials, ensuring meaningful and precise results.

Special Cases and Custom Solutions

QCarbon is also equipped to handle special cases, such as the analysis of single-wall carbon nanotubes (SWCNTs). These materials pose unique challenges, like low D peak intensity and baseline discrepancies. QCarbon offers tailored solutions and multiple processing to align with the user's needs on fitting principles, ensuring accurate and repeatable results.

To closely analyze the D/G ratio of our unknown powder, we spread the powder on a glass slide and mapped a 50 µm x 50 µm area with 1 µm steps. Raman mapping was conducted using the high-performance XploRA™ PLUS microRaman instrument. The raw mapping data was directly sent to the QCarbon application, where it was processed and analyzed automatically in only a few seconds.

The software displays three Raman images, as shown in the graph below. The first two show the intensity, width, or area of the D band and G band respectively. The third image represents the ratio of the intensity, width, or area of D to G. These maps reveal that the carbon powder sample is heterogeneous, with a mixed distribution of ordered and disordered regions. The degree of disorder varies across the sample, with some areas exhibiting high defect density and others showing more ordered carbon structures. This suggests a non-uniformity in the structural properties of the carbon material.

We also obtained statistics about the distribution of intensity, width or ratio of D band, G band, or the D/G ratio. As we are interested in the intensity ratio, we study the histogram of ratio, displayed in the figure below. We see that 80% of the D/G ratios are between 0 and 0.5 (30% < 0.2 and 50% between 0.2 and 0.5), indicating that most of the mapped area has a relatively low level of disorder. In contrast, 20% of the D/G ratios are greater than 0.5, indicating that a smaller portion has a higher degree of disorder. This analysis suggests that the powder is predominantly graphitic with a low level of disorder.

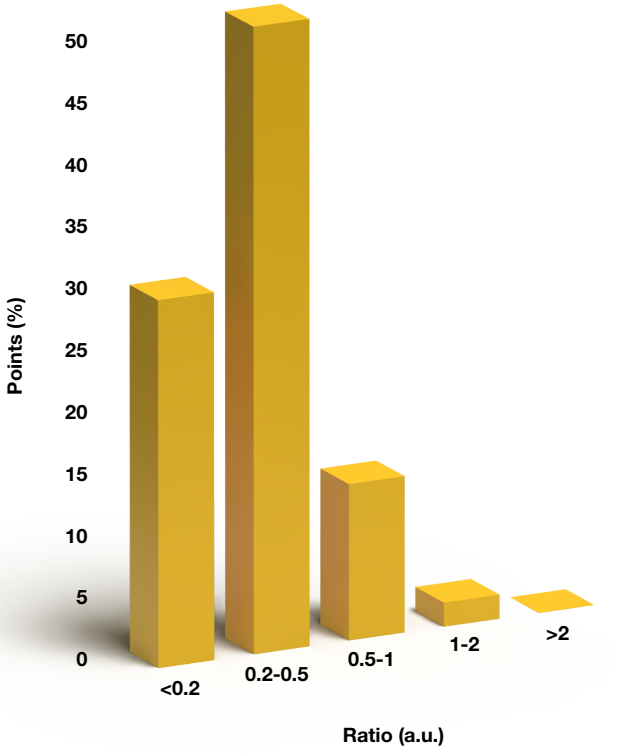


Figure 6: Histogram of D/G intensity ratio

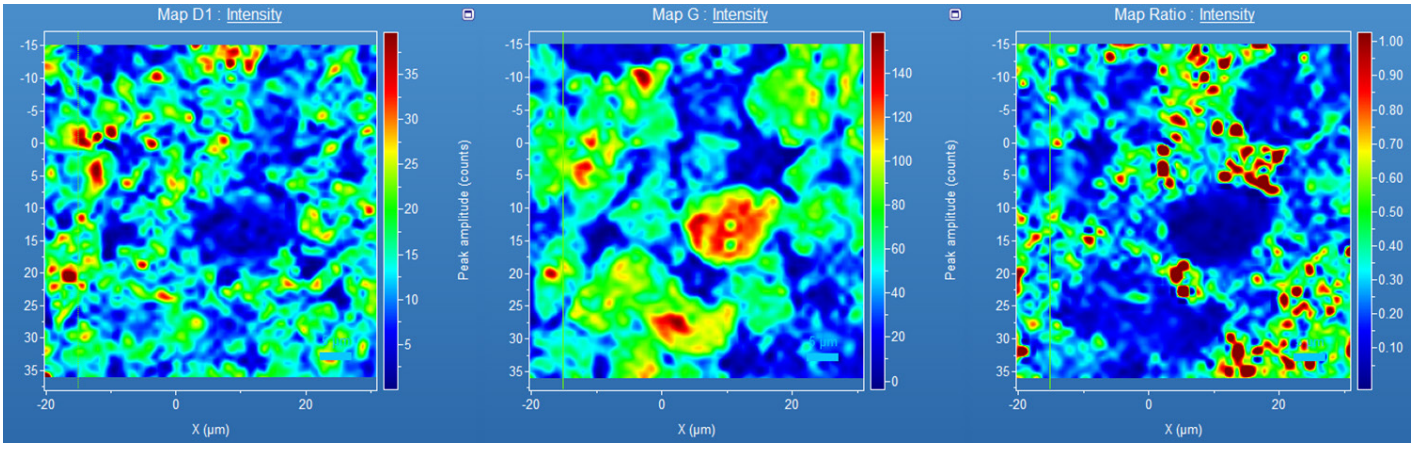


Figure 5: Raman maps of the carbon powder. Map D1 shows the intensity of the D band, Map G shows the intensity of G band, and Map Ratio shows the ratio of D band intensity over G band intensity

Through our QCarbon analysis, we gained detailed insights into the structural properties of the carbon powder sample, showcasing the tool's precision and efficiency. By utilizing advanced Raman spectroscopy and a sophisticated 5-peak fitting technique, we accurately distinguished between ordered and disordered regions within the sample. This analysis confirms that the carbon powder is predominantly graphitic with low disorder, underscoring QCarbon's ability to deliver comprehensive and accurate characterization, making it an invaluable asset for industries reliant on high-quality carbon materials.

Conclusion

The analysis of carbon materials is critically important across various industries due to the unique properties and performance capabilities of these materials. Ensuring precise and efficient analysis is vital for maintaining high standards of quality and advancing technological innovations. HORIBA's ParticleFinder™, along with QCarbon, provides a comprehensive and rapid solution for the detailed characterization of carbon materials.

ParticleFinder™ app, paired with the XD-100 Particle Disperser, offers a high-throughput solution for carbon particle analysis. It automates particle location, characterization, and Raman analysis, efficiently processing large volumes of data.

QCarbon's advanced 5-peak fitting method, automated reporting capabilities, and adherence to industry standards ensure reliable and accurate analysis. By streamlining the QC process and reducing manual intervention, QCarbon significantly enhances productivity and decision-making speed.

With these tools, HORIBA delivers a full turnkey solution that meets the complex needs of modern industries, supporting ongoing advancements in material science and quality control. HORIBA continues to set new standards in the field, offering robust, user-friendly solutions that drive progress and innovation in carbon material analysis.

References

1. HOLMES, Mark. Global carbon fibre market remains on upward trend. Reinforced Plastics, 2014, vol. 58, no 6, p. 38-45.
2. BOKOBZA, Liliane, BRUNEEL, Jean-Luc, et COUZI, Michel. Raman spectra of carbon-based materials (from graphite to carbon black) and of some silicone composites. C, 2015, vol. 1, no 1, p. 77-94.
3. OKUDA, Haruki, YOUNG, Robert J., WOLVERSON, Daniel, et al. Investigating nanostructures in carbon fibres using Raman spectroscopy. Carbon, 2018, vol. 130, p. 178-184.
4. SADEZKY, Alexa, MUCKENHUBER, Harald, GROTHE, Hinrich, et al. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. Carbon, 2005, vol. 43, no 8, p. 1731-1742.

HORIBA

info.sci@horiba.com

www.horiba.com/scientific

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606
France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 (80) 4127 3637
Brazil: +55 (0)11 2923 5400
Germany: +49 (0) 6251 8475 0
Japan: +81(75)313-8121
Singapore: +65 (6) 745-8300
Other: +33 (0)1 69 74 72 00