

Bio-Solubilisation-Induced Graphitization of Coal

***Dr. Deepa Saxena**

Abstract

In this research study we examine the potential of bio-solubilization as a new strategy to cause graphitization in coal. Using a Raman spectrometer with an excitation wavelength of 514.5 nm, the Raman spectra of two coal samples of various rankings were examined. It was found that the first-order dispersion of the E_{2g} mode, the G band, was present. The D band, which first emerged at around 1355 cm⁻¹, provided evidence for edge planes and chaotic materials. The G, D1, D2, D3, and D4 bands were identified by analysis of the curve fit. Indicating the presence of faults in the graphene layers, the integrated intensity ratios (IG/ID') and ID/ID' ratios for bituminous and sub-bituminous coal, respectively, were determined to be 3.66 and 5.8 and about 3 and 4.9, respectively. The second-order spectrum analysis identified the G*, G', D + D', and 2D' peaks in the 2D band, which were measured at 2445, 2690, 2925, and 3160 cm⁻¹, respectively. The sub-bituminous coal sample comprised 6–8 stacked layers of graphene, according to analyses of the second-order spectrum. These findings have profound consequences for the structural qualities of coal samples with different ranks and provide crucial information about those qualities.

Introduction

Due to its applications in a variety of sectors, such as electronics, energy storage, and materials science, graphitization—the process by which coal is converted into a graphitic substance predominantly composed of carbon—holds enormous relevance. Traditional techniques of graphitization, however, require either severe chemical treatments or energy-intensive procedures.

Graphene is a sp² monolayer allotrope of carbon that may be layered to create fullerenes, nanotubes, and graphite. The manufacture of carbon from cheap and abundant natural sources like coal has captivated many researchers in the last few years with the discovery and development of numerous carbon allotropes. The anaerobic digestion of plant material and other organic components results in the mineral known as coal. It consists mostly of extremely disordered amorphous carbon and crystalline carbon with random layer structure. About 3–4 carbon layers are layered in the graphite-like crystalline domain, with an interlayer spacing of 0.35 nm and a stacking height of 3 nm. The amorphous worlds are made up of organic materials and heterocyclic aromatic compounds with an uneven onion-like organization, akin to graphene sheets. The physicochemical makeup of coal, its constituent composition, and graphitization are all influenced by its rank and the formational circumstances. Raman spectroscopy is more suited for characterizing disordered materials than X-ray analysis is for characterizing ordered materials like graphite. Raman spectroscopy has several uses in

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analyzing the structural characteristics of amorphous carbons and has significant promise for characterizing them. By offering insightful information on flaws, It contributes significantly to understanding the structure of graphitic materials by the stacking of graphene layers and the small size of crystallites. High intensity, precise placement, and shape Raman peaks provide vital information about various carbon structure types. Due to lattice vibrations that are sensitive to the level of disorder, there are significant differences between the Raman spectra of perfect graphite and severely disordered graphite. By utilizing Raman spectroscopy to look at the natural organic content of carbon compounds, including coal, several investigations have connected Raman bands to the structural order of amorphous carbons. Raman spectroscopy research was carried out by Balachandaran et al. to demonstrate the existence of graphite-like carbon in charcoal, coal, and carbon black. The G band, which is approximately 1580 cm^{-1} , has often been associated with crystalline graphite, but the D bands, which are between 1100 and 1500 cm^{-1} , are associated with structural disorder within the graphitic framework. Raman spectroscopy has helped coal analysts better understand how char forms in coal under varied gasification and temperature conditions. It hasn't yet reached its full potential for research on coal and other amorphous carbons.

This study's goal was to determine if Raman spectroscopy is appropriate for examining coal's structural characteristics. The Raman spectra of two samples of bioleached coal were investigated using methodical spectral studies. The researchers were able to determine spectral parameters and get important details about the samples' structural properties by deconvoluting the first and second order spectra.

Methodology

In this work, bituminous coal and sub-bituminous coal samples were used to examine the production of monolayers using Raman spectroscopy. For a period of 10 days, *Aspergillus niger* fungus were used in a potato dextrose medium to bioleach the coal samples. You may find the specifics of the bioleaching procedure in earlier papers by the same authors. After bioleaching, the aggregated particles were dissolved in water and sonicated at a frequency of 33 MHz for 30 minutes. Using a Micro Raman Spectrometer (Horiba Jobin Lab RAM HR system) with an excitation wavelength of 514.5 nm, the samples were separated and then evaluated for morphological traits. The spectrum analysis and curve fitting were performed using Origin 8, a computer application.

Results and Discussion

Although they are quite different from those observed in traditional graphene systems, similar patterns may be detected in the Raman spectrum of bituminous and sub-bituminous coal. The coal samples have a large, overlapping, strong graphitic band (G) at 1571 cm^{-1} and a defective band (D) at 1376 cm^{-1} , in contrast to graphene. The defect band's expansion suggests a greater defect presence even while the graphitic band is mostly unaltered. Only a modulated bump is seen in the 2D area ($3250\text{-}2400\text{ cm}^{-1}$), which is different from the narrow peak seen in graphene or the multiple peaks seen in graphite. The sp^2 carbon network's E_{2g} symmetry is thought to be responsible for the G band's strong Raman activity. The D band, on the other hand, is connected to sp^3 carbon and

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indicates the existence of flaws that are uncommon in highly crystalline graphite. A common metric for determining the degree of defect in graphitic materials is the integrated intensity ratio of the D band to the G band (I_D/I_G). This ratio is determined to be 0.84 in the case of coal, pointing to a comparatively low level of disorder in the graphitic structure. While the presence of defects (D band) is mostly restricted to regions where the crystallite structure is defective, such as around the margins, the intensity of the G band seems consistent across the bulk of the material.

The spectrum also reveals the existence of D and D' peaks, which are indicative of defect-induced Raman characteristics uncommon in highly crystalline graphite and appear alongside the G and 2D bands. The existence of delocalized states near the sp^2 chains causes the D band to manifest at 1376 cm^{-1} . The intensity ratio (I_D/I_D') supplies information about the kind and distribution of defects. The G peak may be seen as a little shoulder to the D' peak, which is often less intense than the D peak. Understanding the type of defect is especially dependent on how prominent the D' peak is. The D' peak, which may be up to one-third as intense as the G peak, becomes more distinct as the disorder concentration increases. For bituminous and sub-bituminous coal, the G peak to the D peak ratio (I_G/I_D') is predicted to be between 3.66 and 5.8, while the I_D/I_D' ratio is predicted to be between 3 and 4.9. These findings suggest that the graphene system in coal demonstrates both the on-site and the hopping defects. Coal's graphene layers have a different crystal structure as a result of the out-of-plane bending of sp^3 hybridized carbon atoms.

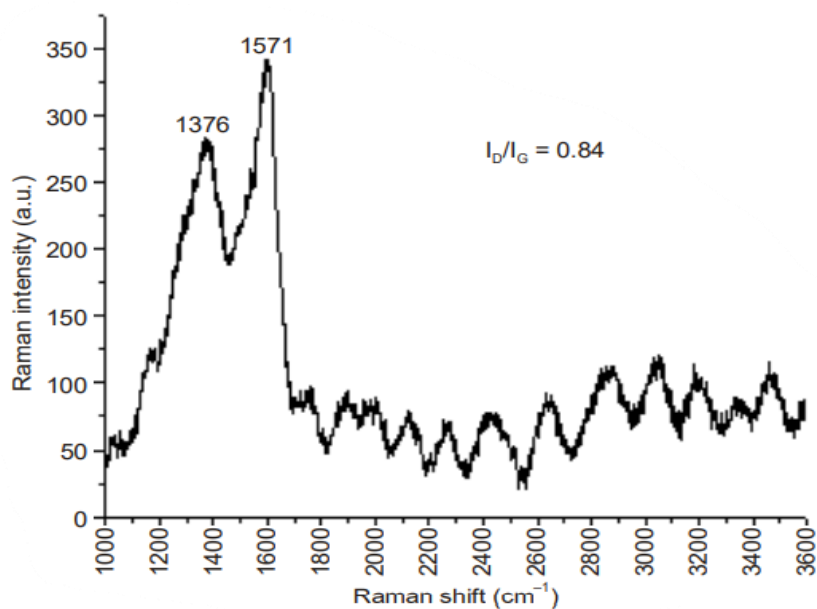


Figure 1. Bituminous coal's Raman spectrum after *Aspergillus niger* bioleaching

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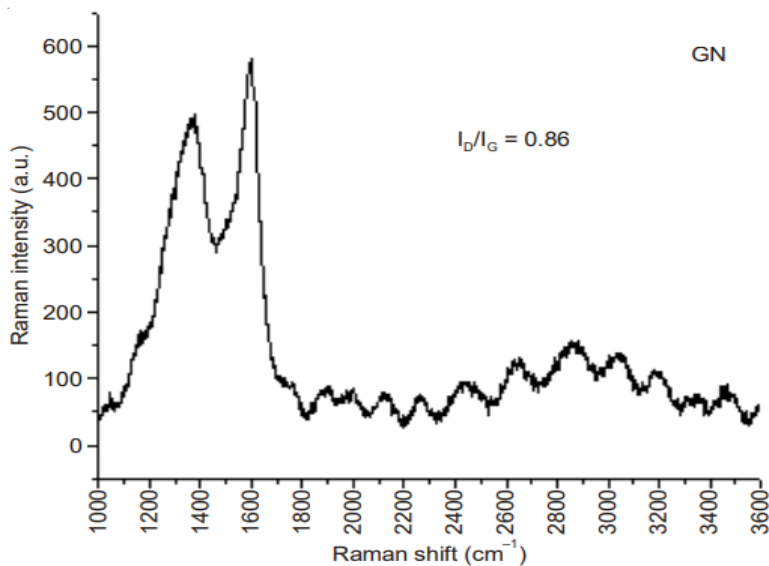


Figure 2. Sub-Bituminous coal's Raman spectrum after *Aspergillus niger* bioleaching

Sub-bituminous coal underwent a similar study, as seen in Figure 2. The E2g mode's association with a structure resembling graphite is confirmed by the G band peak at 1583 cm⁻¹ in the spectrum. It is seen that the D band is very weak, which suggests that the crystal lattice has few flaws. The fault and graphite bands' relative intensity ratio is found to be 0.86. Furthermore, the existence of high-quality carbon nanolayers may be shown by calculating the bituminous coal has aromatic lamellae with a lateral size of 5.24 nm and sub-bituminous coal with a lateral size of 5.11 nm. In the region of around 3600 to 2200 cm⁻¹, a large bump is seen in the spectra of both coal samples (Figures 1 and 2). Notably, unique peaks are seen at around 2750 cm⁻¹ and 2900 cm⁻¹, respectively, which have been linked to the 2D overtone and the combination of G and D bands. The overtone of the graphitic vibration mode with a Raman-inactive frequency of roughly 1200 cm⁻¹ is another band that was seen at around 2440 cm⁻¹.

The position of the G' band indicates the number of layers and the stacking order in the graphite sample. The G* and G' bands may be used to spot changes in the graphitic lattice. It is well known that the 2D peak (G' peak) displays a double-peak shape for a few-layer graphene structure that is precisely stacked (about 6-8 layers). The G' shoulder rises higher and ultimately combines with the G' band to form a single 2D band (the G' band) when disorder levels rise. The development of turbostraticity and the eradication of three-dimensional ordering are blamed for this phenomenon.

Based on curve fitting, spectral analysis: Curve fitting research was done to establish a measurable connection between the coal's structural properties and its Raman spectra. Due to the overlap

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between these two bands, it was found that relying merely on the intensity ratio of the D peak to the G peak does not provide full information. Defects in coal are caused by a variety of disordered carbon material structural properties. However, in extremely amorphous materials, these distinguishing characteristics are hidden at the area where the graphitic and defective bands meet. The Raman spectra were deconvoluted (Figure 3) in order to better comprehend the coal structure. Graphitic lattices are responsible for the strong G peak seen at 1571 cm^{-1} and the D2 band seen at 1609 cm^{-1} . Additionally, the D3 band at 1505 cm^{-1} has a Gaussian line form and is connected to the amount of amorphous carbon in coal, which is consistent with earlier research on amorphous carbon. The D4 band (1280 cm^{-1}), a shoulder peak next to the D band, is thought to result from $\text{sp}^2\text{-sp}^3$ bonding or C-C and C=C stretching. The Raman spectra of certain soot samples have shown a Lorentzian form for this band, according to earlier studies. These peaks may result from the sum and difference of trans-polyacetylene's C=C stretching and CH wagging in nano-crystalline diamond, or they may be an indication of nano graphitic structures, according to certain theories. These results suggest that the coal sample under study may include finite-sized crystalline areas and defect-induced carbon.

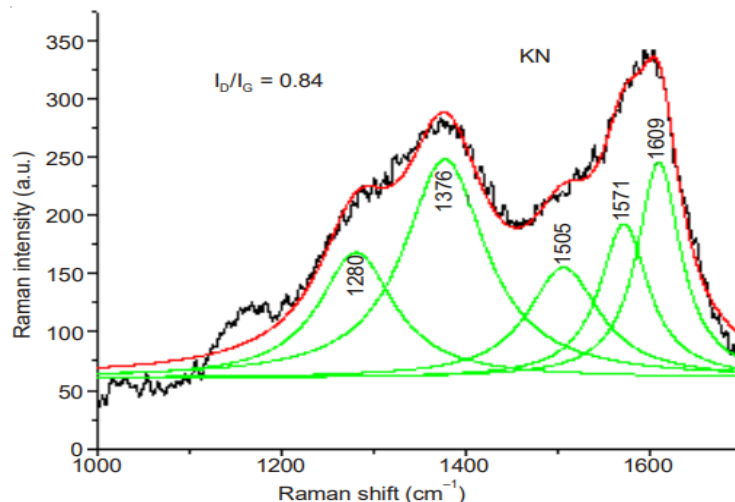


Figure 3. Utilizing curve fitting, analysis of the bituminous coal's first order Raman spectra after being KN-leached with *Aspergillus niger*.

The peak positions observed in bituminous coal and sub-bituminous coal exhibit noticeable similarities. The ratio of defect to graphitic bands (I_D/I_G) for KN and GN is determined to be 0.84 and 0.86, respectively. In order to investigate the effects of structural defects in coal, the 2D region of the Raman spectrum is analyzed by separating its constituent peaks (Fig. 4). A fitting process using multiple Lorentzian profiles is employed to characterize the prominent G^* , G, D+D, and 2D bands, which are observed at 2445 , 2720 , 2925 , and 3160 cm^{-1} , respectively. These peaks arise from the

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splitting of electron dispersion energies resulting from interactions between adjacent graphitic planes. The presence of disorder within the graphene layers may contribute to the observed band, potentially as an overtone of the D band. The positioning of the G band is influenced by factors such as the number of layers and the arrangement of graphite within the sample, providing insights into changes occurring within the graphitic lattice. The behaviour of the 2D peak, typically exhibiting a two-peak shape in well-stacked few-layer graphene, undergoes a shift and eventually combines into a single 2D band as disorder increases. The emergence of turbostraticity and the lack of three-dimensional ordering are both linked to this phenomena. The carbon atoms along the graphene plane's edge are what cause the D band to appear in polycrystalline carbonaceous materials, such as nano graphitic crystallites. The D1 band's and the D2 band's early overtones, commonly known as the G+D band, are represented by the bands that were found at 2720 cm^{-1} and 3160 cm^{-1} , respectively. The absorption at 2445 cm^{-1} may be caused by the first overtone of a graphitic lattice vibration mode that is not Raman active at 1280 cm^{-1} . A sizable hump in the 2D region is caused by the broadening of the D+D bands.

The spectrum analysis of sub-bituminous coal with bioleaching reveals three prominent bands: G*, G, and D. The second-order spectrum indicates the generation of 6-8 stacked layers of graphene in sub-bituminous coal, reflecting its structural ordering.

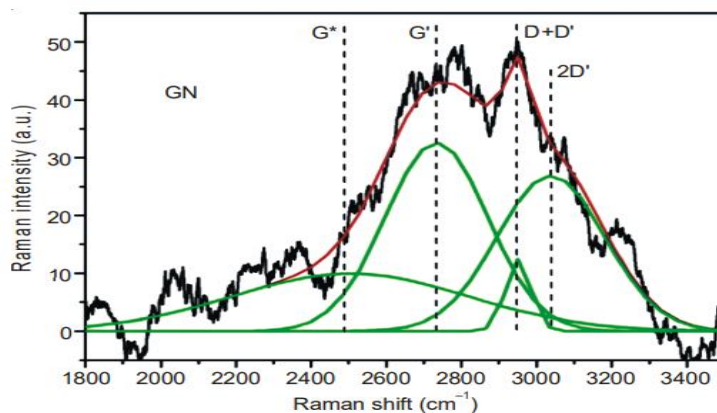


Figure 4: Application of curve fitting analysis to the sub-bituminous coal's second-order Raman spectrum (GN)

The structural alteration brought about by the chemical oxidation process in sub-bituminous coal resulted in a mixed-phase graphene nanostructure with both sp^2 and sp^3 components, as shown by Raman analysis. The presence of a graphitic band and a large defect band indicated a combination of amorphous carbon and nanocarbons that resemble graphene. Furthermore, rather than a purely sp^2 graphene layer; the Raman investigation demonstrated the presence of multi-layer graphene nanosheets comprising a mix of sp^2 - sp^3 components.

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Conclusion

In this study, we looked at the possibility of using coal as a new carbonaceous source for making nanomaterials. Utilizing *Aspergillus niger*, we successfully produced graphene nano carbon structures from both bituminous and sub-bituminous coal utilizing a simple and environmentally friendly fungal solubilization method. Treatment with *Aspergillus niger* facilitated displacement of coal's finite-sized crystalline carbon, resulting in the formation of nanocarbon with an average lateral dimension of around 5.24 nm. We used detailed spectrum analysis and curve fitting techniques to characterize the five distinct bands present in the first-order spectral region. The relative intensities of the defect and graphite bands for bituminous and sub-bituminous coal were determined to be 0.84 and 0.86, respectively. Additionally, we discovered that the ID/ID' ratios for bituminous and sub-bituminous coal were, respectively, between 3 and 4.9 and 3.66 and 5.8, which indicate the presence of both on-site and hopping faults. The second-order spectrum revealed that 6–8 stacked layers of graphene had developed in sub-bituminous coal, but there was no three-dimensional ordering in bituminous coal. Overall, the findings demonstrate that coal has the potential to be a viable starting point for the manufacturing of nanomaterials based on graphene.

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