Graphitization of Coal by Bio-Solubilization: Structure Probe by Raman Spectroscopy

C.D. Elcey[1,*] and B. Manoj[2,*]

[1]Department of Life Sciences, Kristu Jayanti College, Bangalore-560 077, India
[2]Department of Physics, Christ University, Bangalore-560 029, India

*Corresponding author: E-mail: manoj.b@christuniversity.in

Raman spectra of two coal samples of different rank have been examined with Raman spectrometer operating at an excitation wavelength of 514.5 nm. Raman studies manifested the presence of G band conforming the first order scattering of E_{2g} mode. The sp^3 domains at about 1355 cm^{-1} (D band) is an evidence to edge planes and disordered structures. Analysis by curve fitting the first order spectrum justified the presence of G, D1, D2, D3 and D4 bands. The integrated intensity ratio $I_G/I_{D'}$ is found to be 3.66 and 5.8 while the $I_D/I_{D'}$ ratio is estimated to be about 3 and 4.9 for bituminous and sub-bituminous coal, respectively indicating on-site and hopping defect in the graphene layers. The 2D band is fitted with multiple Lorentian profile has 4 peaks, the intense G*, G', D + D' and 2D' band at 2445, 2690, 2925 and 3160 cm^{-1}. From the second order spectrum, formation of about 6-8 stacked graphene layers is observed in sub-bituminus coal.

Keywords: Raman spectroscopy, Amorphous carbon, Defect, Deconvolution.

INTRODUCTION

Graphene is a monolayer allotrope of carbon in sp^2 form, which can be stacked to form graphite, nanotubes or wrapped into fullerenes [1-3]. With the discovery and advance of various allotropes of carbon, its preparation from inexpensive and plentiful natural source like coal has fascinated many researchers in the last few years [4-6]. Coal is a mineral formed by the anaerobic ingestion of vegetal matter and other organic constituents. It comprise crystalline carbon of random layer structure with particular amount of highly disordered amorphous carbon [4]. The graphite like crystalline domain has about 3-4 carbon layers stacked, with stacking height of about 3 nm and interlayer spacing of about 0.35 nm [1,7]. The amorphous realms constituted of heterocyclic aromatic structures, similar to graphene sheets having irregular onion-like arrangement along with other organic components. The physicochemical structure of coal, its elemental composition and graphitization depends on rank and conditions prevailed during formation. For the characterization of ordered materials like graphite, X-ray analysis are the ideal, while for disordered materials, Raman spectroscopy is more suitable [1-3,8-10]. Raman spectroscopy has a potential role in characterization of amorphous carbons and have wide application in its structural investigation. It plays a significant part in the structural elucidation of graphitic materials, by providing valuable details

about defects, stacking of the graphene layers and the finite size of the crystallites. The shape, intensity and position of prominent Raman peaks give significant amount of evidence about diverse types of carbon structures. There is a significant difference between Raman spectrum of ideal graphite and highly disordered graphite. It originates from the lattice vibrations and is sensitive to degree of disorder. Many researchers carried out investigation of Raman character on the natural organic matter in carbon compounds, such as coal and relate the Raman bands to the structural order of the amorphous carbons. Balachandaran *et al*. [11-14] used Raman spectroscopy to establish the existence of graphite like carbon in soot, coal and carbon black. Most of the studies assigned G band (about 1580 cm^{-1}) to crystalline graphite and D bands (1100 to 1500 cm^{-1}) to structural disorder present in the graphitic structure [1-4,8-14]. Raman study has been worthwhile to reveal the evolution of char as a function of temperature and diverse gasification conditions in coal analysis [15]. Raman spectroscopy has not been fully explored for the study of coal and other amorphous carbon [15,16].

In the present investigation, applicability of Raman spectroscopy for the structural depiction of coal by systematic spectral analyses are carried out. The Raman spectra of two bioleached coal samples have been analyzed by de-convoluting the first and second order spectra and the obtained spectral parameters and the structural information are presented.

EXPERIMENTAL

Two different coal samples sub-bituminous and bituminous coal were used as material to investigate the monolayer formation by Raman spectroscopy. The sample was prepared by bioleaching with fungi *Aspergillus niger* in a potato dextrose medium for a period of 10 days (designated as GN and KN, respectively). The details of which are published elsewhere by the same authors [17,18]. The agglomerated particles were dissolved in water and sonicated at 33 MHz for 30 min and separated. The morphological features of samples were analyzed by Micro Raman Spectrometer Horiba Jobin Lab RAM HR system with an excitation wavelength of 514.5 nm in the back scattering mode. Spectral analysis and curve fitting was carried out with the aid of origin 8 software.

RESULTS AND DISCUSSION

The Raman spectra of bituminous coal and sub-bituminous coal (Figs. 1 and 2) have similar patterns but unlike those of the traditional graphene system [1-6,13-16]. It exhibits an intense graphitic band (G) at 1571 cm^{-1} and defective band (D) at 1376 cm^{-1}. They are highly broadened resulting in the overlap of these two bands. The broadening of the defect band is attributed to the enhancement of defect whereas this is rare in graphitic band (G). At the 2D region (3250-2400 cm^{-1}), only a modulated bump is observed [2]. In graphene system, this band appear as narrow peak while in graphite it appears as two peaks. The G band is attributed to E_{2g} symmetry at the Brillouin zone center owing to sp^2 carbon network and is highly Raman active [13-16]. The D-band is attributed to the sp^3 carbon [8-13]. This feature is due to defect and are not observed in highly crystalline graphite. The integrated intensity ratio of the D and G band (I_D/I_G) is widely used parameter for characterizing the quantity of defect in the graphitic materials. This ratio is calculated to be 0.84, indicating low degree of disorder in the graphitic plane of coal [1]. The intensity of G band is found to be uniform over the bulk of the material while the defect (D-band) is confined where the crystallite structure is imperfect (at the edges).

Other than the G and 2D bands, the D and D′ peak is also observed in the spectrum. D and D′ bands are attributed to the defect-induced Raman features, which is absent in highly crystalline graphite. In the spectrum the D band is found at 1376 cm^{-1}, which is due to the delocalised π states around the sp^2 chains. The intensity ratio ($I_D/I_{D'}$) gives the information about nature and concentration of defects). D′ peak have generally low intensity compared to D peak and appears as a small shoulder to G peak. It is of prime importance to investigate the prominence of D′ peak for understanding the type of defect. As the disorder concentration increases, the D′ peak will be well resolved (up to 1/3rd intensity of G peak). The ratio of G peak to D′ peak ($I_G/I_{D'}$) is found to be 3.66 and 5.8 while the $I_D/I_{D'}$ ratio is estimated to be about 3 and about 4.9 for bituminous and sub-bituminous coal, respectively. From these results, it can be concluded that the defect on the graphene system present in coal is combination of on-site and hopping defect. The out-of-plane bending of sp^3 hybridized carbon atom introduces distortions in the crystal lattice of graphene layers of coal.
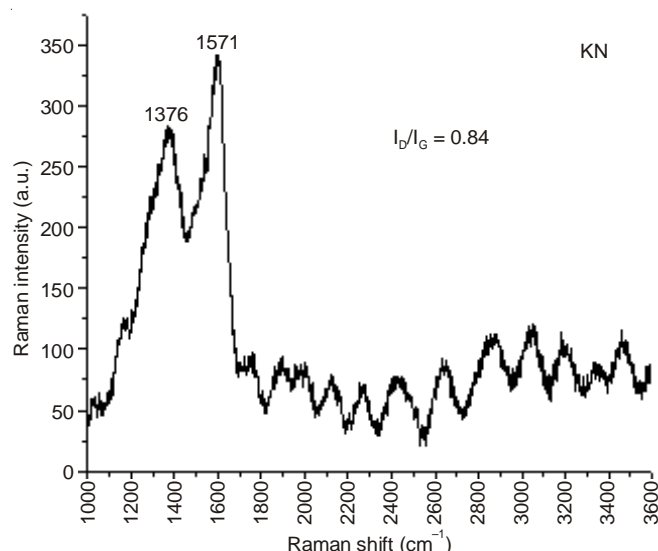

Fig. 1. Raman spectrum of bituminous coal (KN-leached with *Aspergillus niger*)
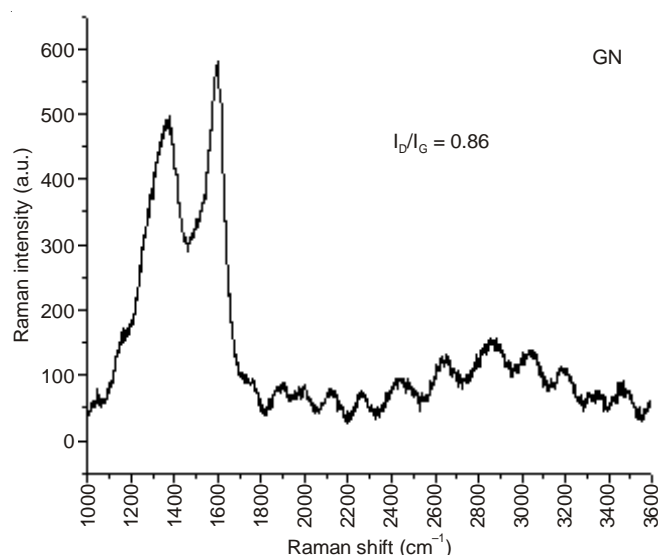

Fig. 2. Raman spectrum of sub-bituminous coal (GN-leached with *Aspergillus niger*)

A similar kind of analysis on sub-bituminous coal is shown in Fig. 2. The peak observed at 1583 cm^{-1}, due to the G band, unveils the presence of E_{2g} mode of graphite like structure. The D band is very weak, indicating low level of defects in the crystal lattice. The relative intensity ratio of the defect and graphite bands was found to be 0.86, while the lateral size of the aromatic lamellae was calculated to be 5.24 and 5.11 nm for the bituminous and sub-bituminous coal, respectively, revealing high quality carbon nanolayers [19,20].

In the spectra, both the coal samples unveiled broad bump in the range of about 3600 to 2200 cm^{-1} (Figs. 1 and 2). The pronounced peaks at about 2750 and 2900 cm^{-1} have been assigned to 2D overtone and G+D combination, respectively [1]. The band at ~2440 cm^{-1} is the overtone of Raman inactive graphitic vibration mode at about 1200 cm^{-1} [1-9].

The G′ band position depends on the number of layers and stacking order of the graphite sample. Any modification of the graphitic lattice is identifiable by the G* and G′ band. It

is reported that, for a perfectly stacked few layer graphene (about 6-8 layers), the 2D peak (G′ peak) exhibits two peak profile. As the disorder increases, the G′ shoulder shift upwards and finally merges into G′ band and results into single 2D band (G′ band). This is due to the advance of turbostraticity and the disappearance of three dimensional ordering.

Spectral analysis by curve fitting: Quantifiable correlation between Raman spectra and structural parameters of coal may not be attained by only considering intensity ratio of D peak to G peak mainly due to the overlap of these two bands [15]. Defects in coal is originating from numerous structural topographies of the disordered carbon materials. For highly amorphous materials, these information is hidden in the overlap between the graphitic and defective bands. In order to acquire more information about the structure of coal,it is essential to deconvolute its Raman spectra (Fig. 3). It is suggested that, the observed G peak (1571 cm^{-1}) and the D2 band (1609 cm^{-1}) arises from graphitic lattices [1-4]. The D3 band (1505 cm^{-1}) originates from the amorphous carbon content of coal and has Gaussian line shape. This is in agreement with the result of Jawahari *et al.* [21,22] in amorphous carbon. The shoulder peak near the D band is designated as D4 band (~1280 cm^{-1}) and which arises due to sp^2-sp^3 bonds or C-C and C=C stretching. Sadezky *et al.* [1] reported a Lorentian shape for this band in the Raman spectra of selected soot samples. Ferrari and Robertson [23] attributed the origin of these two peaks to the sum and difference of C=C stretching and CH wagging of the *trans*-polyacetylene in nano-crystalline diamond. They also could originate from the nano graphitic structure. This suggest the possibilty that, the observed peak in the coal sample is due to the existence of finite size of crystalline and defect induced carbon.
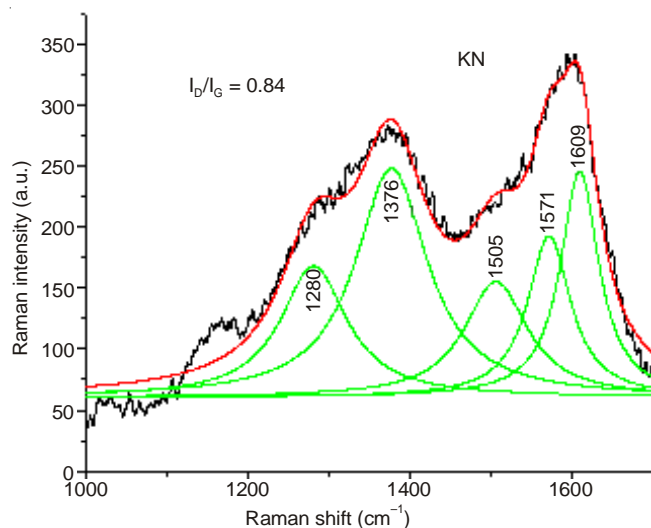
The 2D band is fitted with multiple Lorentian profile has 4 peaks, the intense G*, G′, D+D′ and 2D′ band at 2445, 2720, 2925 and 3160 cm^{-1}. This is attributed to the splitting of π electron dispersion energies caused by the interaction between neighboring graphitic planes [22-24]. This band also could be due to the overtone of the D band and credited to the induced disorder in the graphene layers. The position of the G′ band depends on the number of layers and stacking order of the graphite sample. Any modification of the graphitic lattice is identifiable by the G* and G′ band. It is reported that, for a perfectly stacked few layer graphene (about 6-8 layers), the 2D peak (G′ peak) exhibits two peak profile [24]. As the disorder increases, the G′ shoulder shift upwards and finally merges into G′ band and results into single 2D band (G′ band). This is due to the advance of turbostraticity and the disappearance of three dimensional ordering. In polycrystalline carbonacoues materials, having lot of nano graphitic crystallites, carbon atoms at the boundary of the graphene plane act as the source of the D band. The band at 2720 cm^{-1} is originates from the first overtone of the D1 band while band at 3160 cm^{-1} is assigned to the first overtone of D2 band or G+D′ band. The absorption at 2445 cm^{-1} could be due to first overtone of a Raman-inactive graphitic lattice vibration mode at 1280 cm^{-1} [22-24]. The D+D′ bands are broadened resulting in a broad bump in the 2D region. The spectral anlysis (Fig. 4) reveals sub-bituminous coal shows three prominent bands- G*, G′ due to the structural ordering of sub-bituminous coal with bio leaching. From the second order spectrum, it is evident that in sub-bituminous coal about 6-8 stacked graphene layers are formed.
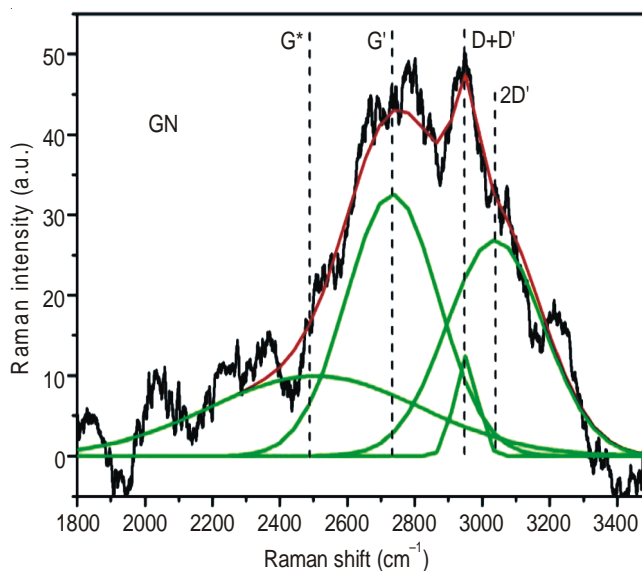

Fig. 3. Curve fit for the first order Raman spectrum of bituminous coal (KN-leached with *Aspergillus niger*)

Fig. 4. Curve fit for the second order Raman spectrum of sub-bituminous coal (GN)

A broad similarity in the peak position is noticed in the spectrum of bituminous coal with sub-bituminous coal. The ratio of defect to graphitic band (I$_D$/I$_G$) is found to be 0.84 and 0.86 for the KN and GN, respectively.

To understand the influence of defects in the structure of coal, 2D region is deconvoluted into constituent peaks (Fig. 4).

Thus, Raman analysis showed that after chemical oxidation the structure of carbon in sub-bituminous coal was converted into a mixed phase graphene nanostructure containing both sp^2 and sp^3 components. The presence of graphitic band and a broad defect band showed that it is a combination of amorphous and graphene like nanocarbon. Raman analysis also confirms the presence of multi-layer graphene nanosheets that contain mixed phase sp^2-sp^3 components than a pure sp^2 graphene layer.

Conclusion

Coal is a novel carbonaceous material whose utility as a potential precursor for nanomaterial is least explored. Herein we report a simple and ecofriendly fungal solubilization method to fabricate graphene nano carbon structure from bituminous and sub-bituminous coal. The finite size crystalline carbon in coal is easier to displace with *Aspergillus niger* leaching, leading to formation of nanocarbon with lateral dimension of about 5.24 nm. The spectral analysis by curve fitting justified the evidence of five bands in the first order spectral region. The relative intensity ratio of the defect and graphite bands was found to be 0.84 and 0.86, for the bituminous and sub-bituminous coal, respectively. The ratio of G peak to D′ peak ($I_G/I_{D'}$) is found to be 3.66 and 5.8 while the $I_D/I_{D'}$ ratio is estimated to be about 3 and about 4.9 for bituminous and sub-bituminous coal, respectively confirming on-site and hopping defect. From the second order spectrum, formation of about 6-8 stacked graphene layers is observed in sub-bituminous coal while in bitumionus coal the three dimensional ordering is disappeared.

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