

*Short Communication*

## **Raman Spectroscopy Investigation of Camphor Soot: Spectral Analysis and Structural Information**

*Ramya , Krishnan. Jerin John and B. Manoj*

Dept.of Physics, Christ University, Bangalore-29, Karnataka, India

E-mail: [manoj.b@christuniversity.in](mailto:manoj.b@christuniversity.in)

*Received:* 12 April 2013 / *Accepted:* 31 May 2013 / *Published:* 1 July 2013

---

Raman spectra of camphor soot has been investigated and optimised with a Raman microscope system operated at laser excitation wavelength of 514.5 nm. Several band combinations for spectral analysis have been tested, and a combination of three Lorentian bands ( G,D1,D2) at about 1580, 1350 and 1620  $\text{cm}^{-1}$ , respectively, with Gaussian-shaped band (D3) at 1500  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  (D4) was best suited for the first order spectra. The second-order spectra were best fitted with Lorentian shaped bands at about 2450, 2700, 2900 and 3250  $\text{cm}^{-1}$ . The results are discussed and compared with X-ray diffraction measurements and SEM analysis. The camphor soot shows  $\gamma$  and  $\Pi$  bands which reveals the presence of crystalline graphitic carbon. The SEM micrographs of camphor show the presence of carbon nanostructures.

---

**Keywords:** Raman spectroscopy, Carbon nanospheres, X-ray diffraction, Camphor soot

### **1. INTRODUCTION**

Allotropes of carbon have been a subject of great interest among researchers for several decades. Amorphous carbon is the broad name used for coal, soot and other impure forms of the element [1-3]. Soot is the black solid formed by the partial combustion or pyrolysis of fossil fuels and organic materials. It is primarily composed of carbon and consists of agglomerated particles with diameter of about 10-30 nm. They have neither graphite nor diamond like structures. The graphite-like crystalline domain typically consist of 3-4 turbostratically stacked graphene layers, with average lateral size of  $\sim 3$  nm and interlayer distances of about 3.5Å, and are considered as highly disordered graphitic lattice [1-4]. In an ideal graphitic lattice, the distance between parallel graphene layers is 3.34Å, and the layers are arranged in alternating sequence [3-5]. Amorphous carbon has a wide range of properties that are primarily controlled by the different bond hybridizations possible in such

materials. They are composed of polycyclic aromatic compounds, which are regarded as graphene layer precursors in irregular arrangements, and other organic and inorganic components [6].

For the structural characterization of highly ordered crystalline solid materials X-ray diffraction techniques are usually adapted [1-5]. For disordered materials like soot, Raman spectroscopy is promising tool, because it is sensitive not only to crystal but also to short range molecular structures. It is known fact that the Raman reflection of graphite crystals results from lattice vibrations and are very sensitive to the disorder. Among the substances investigated by many research group are different types of graphite [1-7], diamond films [8], glassy carbon, coal [1-3] and fullerenes. Several studies have reported the presence of graphite like carbon in diesel and kerosene soot. Kumar and Ando produced carbon nanotubes from Camphor- a botanical hydrocarbon [4]. It is also reported that the different types of soot could be distinguished by their degree of graphitization [1-5]. In the present study, structural characterization of camphor soot has been done using different analytical methods like Raman spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS). The Raman spectra have been analyzed by curve fitting with different band combinations, and the obtained spectral parameters and their structural information are discussed. X-ray scattering is used to obtain information on the atomic scale, especially the average carbon-carbon distance and the average coordination number of the carbon atoms. SEM study reveals information such as external morphology, chemical composition, and orientation of materials making up the sample. With these analytical methods one could calculate the structural parameters like aromaticity ( $f_a$ ), lateral size ( $L_a$ ), stacking height ( $L_c$ ) and number of carbon per aromatic lamellae [1-6].

## 2. EXPERIMENTAL

The morphological features of nanomaterials were analyzed by SEM-EDS and XRD. The surface morphology and EDS measurements were obtained by Scanning Electron Microscope (SEM) model JSM 6390 from JEOL Company in Japan. The XRD measurements were carried out using a Bruker AXS D8 Advance X-ray diffractometer. The camphor soot was prepared by the thermal decomposition of camphor in open air. Raman spectral investigation was carried out using Horiba Jobin LabRAM HR system with an excitation wavelength of 514.5 nm.

## 3. RESULT AND DISCUSSION

### 3.1. Characterization of Amorphous Carbon from Camphor Soot

Camphor, a botanical hydrocarbon, which on burning undergoes thermal decomposition to form soot. Atmospherically burned camphor produces thermolytic particles which are extremely small. The EDS analyses of soot (Figure.1) revealed the presence of carbon (93.29%), oxygen (3.19%), aluminum (0.63%), silicon (0.55%) and potassium (2.34%).

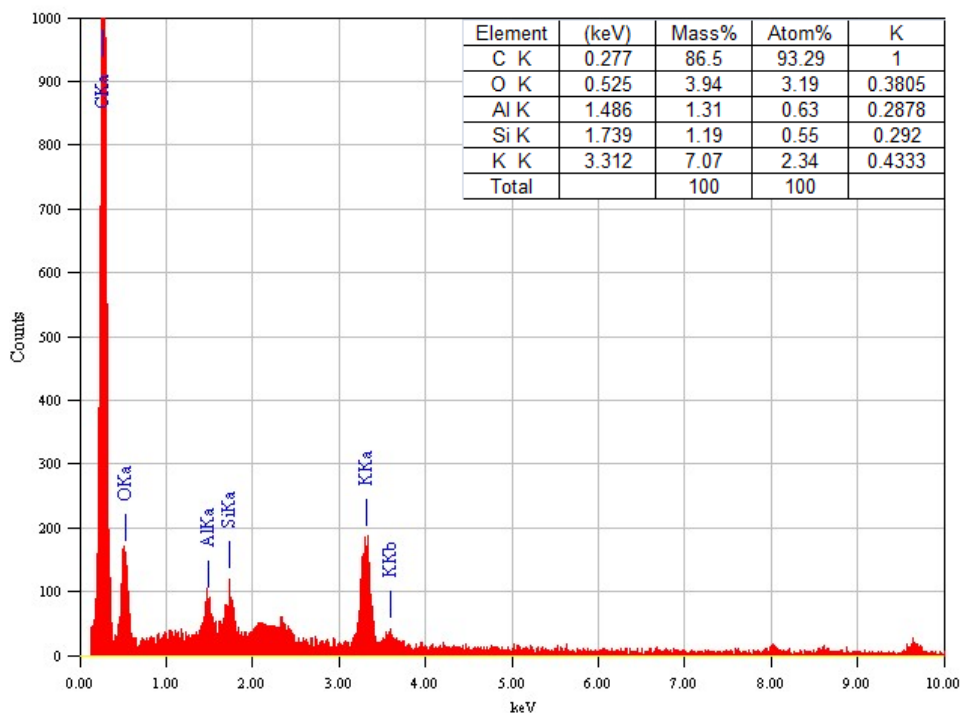


Figure 1. EDS data of Camphor

The SEM micrograph of nanomaterials formed from camphor is presented in Figure 2. The surface morphology of the carbon deposit is found to be non uniform. The SEM images revealed that particles of carbon are in the form of spheres of about 70-90 nm diameter. Large surface area and low resistivity of CNTs makes them of great interest in electrochemistry. CNTs could be very useful for the storage of hydrogen, a key aspect of the clean energy economy.

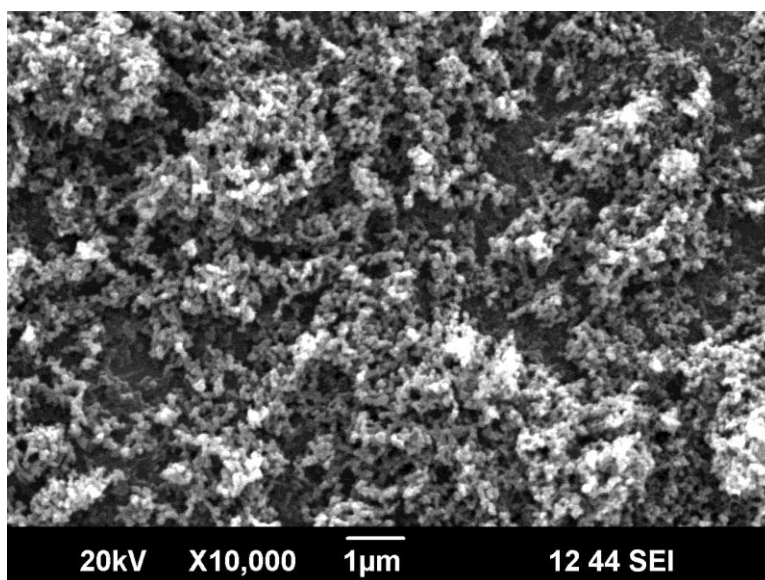


Figure 2. Morphology of camphor soot

### 3.2. X-ray diffractogram of Camphor Soot

A comparative study of the XRD profiles of the camphor soot along with pure graphite is shown in Fig.3. A strong and broadened  $\Pi$  band is observed at  $\sim 25.5^\circ$ , suggesting that the carbon nanosphers (CNS) formed is composed of crystalline graphitic carbon. The ratio of intensity of disorder carbon to ordered carbon ( $I_{20}/I_{26}$ ) is given in table.1. A higher intensity ratio would indicate a higher degree of disorder in the nanostructures. The intensity ratio of the two peaks ( $I_\gamma/I_\Pi$ ) for camphor soot is found to be 0.16. This low value indicates carbon nanomaterials formed are high in quality [4]. Aromaticity of the nanomaterials formed from camphor is determined to be 0.91. [Table.1] The crystallite size ( $L_a$ ) and stacking height ( $L_c$ ) of the sample are determined by using the Scherrer equation [1-2,5,12].

$$L_a = 1.84\lambda / B_a \cos(\phi_a)$$

$$L_c = 0.89 \lambda / \cos(\phi_c)$$

Where  $\lambda$  is the wavelength of the radiation used,  $B_a$  and  $B_c$  are the width of the (100) and (002) peaks, respectively, at 50 % height, and  $\phi_a$  and  $\phi_c$  are the corresponding scattering angles. The  $L_a$  and  $L_c$  values are found to be 89.13 and 23.39 Å respectively for the camphor soot. The  $d_{002}$ -spacing of the lamellae is found to be 3.359 Å which is close to the value of graphite layer reported in various studies [1-2]. Many authors's reported the presence of peak at  $\sim 42.33^\circ$  to hexagonal graphite lattice of multi-walled carbon nanotubes [1-2, 10]. Very weak peak at  $42.33^\circ$  observed in the present study is an indication formation carbon nanomaterial in the soot.

The graphitization degree (G) of the sample was calculated by the equation

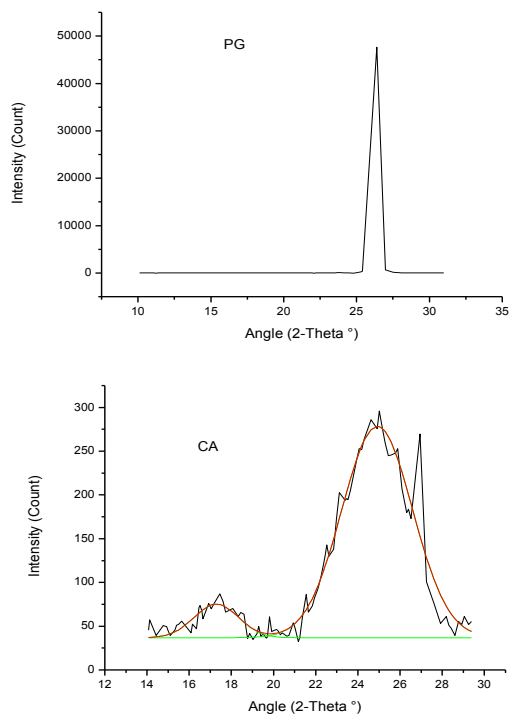
$$G = (0.3440 - d_{002}) / (0.3440 - 0.3354) \times 100\%$$

Where  $d_{002}$  is the interlayer spacing of (002) plane obtained from the XRD patterns [5]. This value is calculated to be 94% in the present investigation. The high degree of graphitization was accompanied by appearance of peaks at (100), (004) and (110) in the XRD pattern.

The mechanism of nanostructure formation in camphor soot is discussed below. The nanostructure formation takes place by adding up of hexagonal and pentagonal rings as building blocks, not individual carbon atom. These radicals are in highly active state and capable of forming a stable structure among them. The temperature generated during the combustion of camphor plays a vital role in the formation of graphene layers. The retention time of the  $sp^2$  carbon atoms in the reaction core is not sufficient enough to form multi-layer graphene (graphite). Instead, only few-layer graphene is kinetically favored.

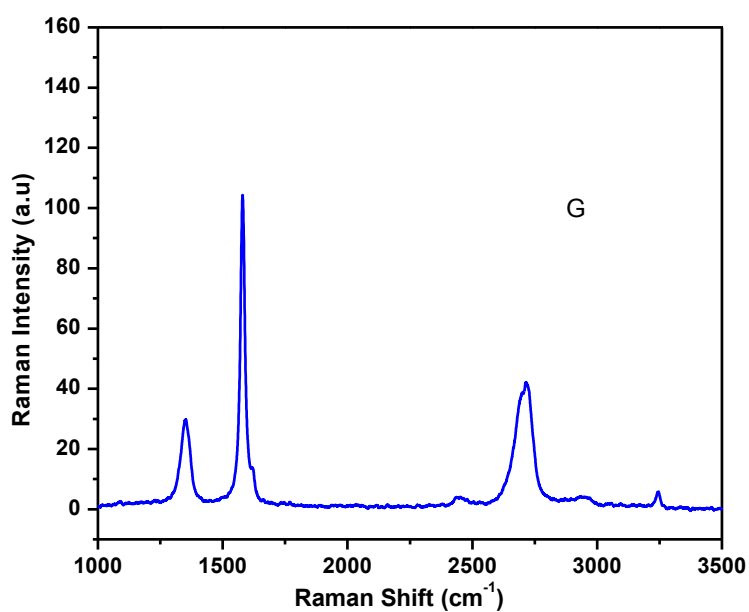
**Table 1.** Structural parameters of camphor soot derived from X-ray analysis

Sample	$I_{26}/I_{20}$	$I_{20}/I_{26}$	$f_a$	$L_a$ (Å)	$L_c$ (Å)	$d_{002}$ (Å)	G
CA	6.30	0.16	0.91	89.13	23.39	3.359	94%



**Figure 3.** XRD data analysis of camphor soot and pure graphite (PG).

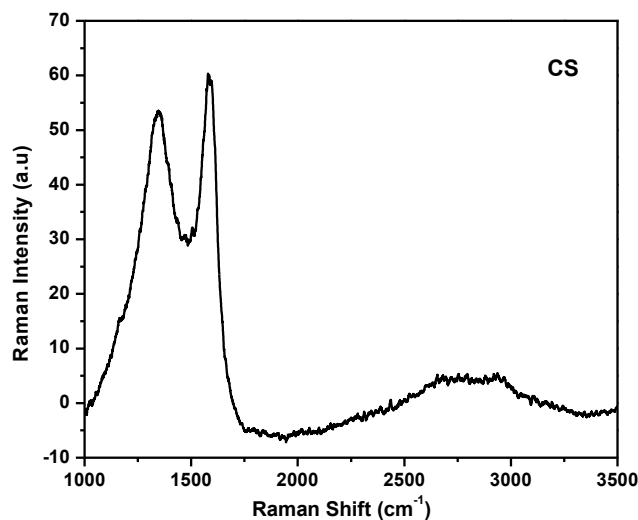
### 3.3. Raman spectra of graphite



**Figure 4.** Raman spectra of pure graphite (PG).

The Raman spectrum of pure graphite (Figure.4) exhibits first-order band, the G-band (Graphite) at around  $1580\text{ cm}^{-1}$  and is due to an ideal lattice vibration mode with  $E_{2g}$  symmetry [1,8-9]. The spectrum exhibits additional first order bands (D or defect band), which are due to characteristic disorderd graphite, which show an increase in intensity relative to the G band as the disorder in the graphitic structure increases. The most intense of them is D1 band, which appears at  $1350\text{ cm}^{-1}$  and is assigned to the graphitic lattice vibration mode with  $A_{1g}$  symmetry. Another disorder band is observed at  $1606\text{ cm}^{-1}$ , which is designated as D2 band, appears as a shoulder with G band. Many authors attributed this band to graphitic lattice mode with  $E_{2g}$  symmetry [6-7]. It is also reported that, for an ideal graphitic crystal, only a few vibrational modes are Raman active. When structural disorder is present, some forbidden vibrational modes become Raman active. In polycrystalline carbonacoues materials consisting of large number of small graphitic crystallites, carbon atoms at the edge of the graphene layers are considered as the most probable origin of the D band [6-7]. The Raman spectra exhibited second order bands at about  $2450\text{ cm}^{-1}$ ,  $2700$  and  $3250\text{ cm}^{-1}$ . The band at  $2720\text{ cm}^{-1}$  is attributed to the first overtone of the D1 band whereas band at  $3250\text{ cm}^{-1}$  is assigned to the first overtone of D2 band. The absorption at  $2450\text{ cm}^{-1}$  can be due to the Raman-active first overtone of a Raman-inactive graphitic lattice vibration mode at  $\sim 1200\text{ cm}^{-1}$  [6].

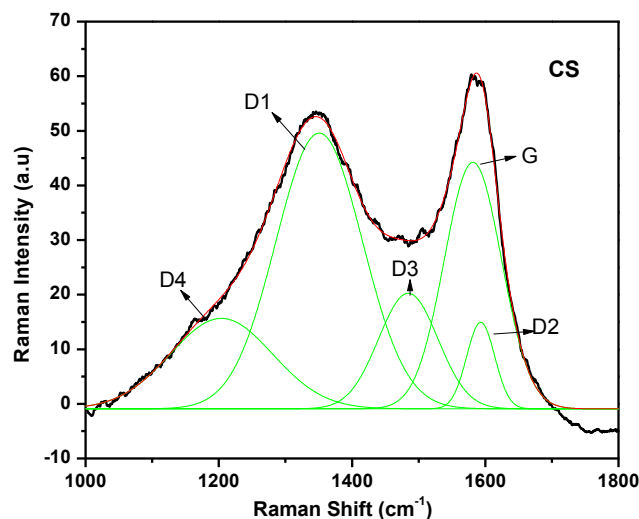
#### 3.4. Raman spectra of camphor soot



**Figure 5.** Raman spectra of camphor soot (CS)

Raman spectra of camphor soot with a laser wavelength of  $\lambda_0 = 514.5\text{ nm}$  is presented in Fig.5. There are two broad and strongly overlapping peaks with intensity maxima at  $1345\text{ cm}^{-1}$  and  $1585\text{ cm}^{-1}$ . These bands are the same D and G bands, which are reported in graphite sample [1-8]. A detailed analysis of first-order Raman bands by curve fitting is carried out. It is found that, the first order spectrum consists of as many as five bands namely G, D1, D2, D3 and D4 bands. Many authors suggested that the peak at  $1585\text{ cm}^{-1}$  comprises not only the G band but also D2 band known from

graphitic lattices [10-16]. In the present study, camphor soot exhibited a peak at  $1605\text{ cm}^{-1}$  clearly supporting the inclusion D2 band.



**Figure 6.** Curve fit for the first-order Raman spectra of camphor soot

The band appeared at  $\sim 1500\text{ cm}^{-1}$  has been designated as D3 band and originates from the amorphous carbon fraction of soot (organic molecules, fragments or functional groups). Jawhari et al. [8] proposed Gaussian line shape for this band due to a statistical distribution of amorphous carbon on interstitial places in the disturbed graphitic lattice of soot. The spectral analysis presented in the present investigation support this finding. The peak at  $\sim 1350\text{ cm}^{-1}$  exhibit a shoulder at  $\sim 1200\text{ cm}^{-1}$ , which is denominated as D4 band. Dippel et al. [16] reported this band at  $\sim 1190\text{ cm}^{-1}$  in the Raman spectra of flame soot and attributed to  $sp^2$ - $sp^3$  bonds or C-C and C=C stretching of vibrations of polyene-like structures. Sadesky et al. [7] reported a Lorentian shape for the band at  $\sim 1180\text{ cm}^{-1}$  in the Raman spectra of selected soot samples. This band shows a normal shape in the present investigation. The second-order bands of the recorded spectra shows bands at the positions  $2450\text{ cm}^{-1}$ ,  $2700\text{ cm}^{-1}$  and  $3250\text{ cm}^{-1}$ , similar to graphite confirming the presence of graphite like carbon in soot.

#### 4. CONCLUSIONS

The camphor soot shows presence of  $\gamma$  and  $\Pi$  bands, indicating the presence of crystalline graphitic carbon. The SEM micrographs of camphor reveal the agglomeration of carbon nanostructures. The EDS analysis confirms the presence of carbon, oxygen along with aluminum, silicon and potassium. The spectral analysis by curve fitting provide the evidence of G, D1, D2, D3 and D4 band in the first-order spectral region. The band D3 and D4 follows Gaussian shape whereas G, D1 and D2 show Lorentian. The soot derived from camphor revealed the formation of second order Raman spectrum like that of graphite.

#### ACKNOWLEDGEMENT

The authors are indebted to the Centre for research, Christ University for providing research grant to carry out this work.

#### References

1. B. Manoj, Kunjomana A G. *Int. J. Min. Met. and Mats.* 19(4), (2012) 279.
2. Anu N Mohan, B. Manoj. *Int. J. Electrochem. Sci.* 7, (2012) 9537.
3. H. Darmstadt, C. Roy, Serge kaliaguine, Guoying Xu, Michele Auger, Alain Tuel, Veda Ramaswamy. *Carbon*, 38, (2000) 1279.
4. M. Kumar, Y. Ando. *Diamond and Related Materials* 12, (2003) 1845.
5. T. Ungar, Jeno Gubicza, Gabor R, Cristian Pantea. *Carbon* 40, (2002) 929.
6. B. Manoj, Kunjomana A G. *Int. J. Electrochem. Sci.* 7, (2012) 3127.
7. Quan Zhou, Zongbin Zhao, Yaring Zhang, Bo Meng, Anning Zhou, Jieshan Qiu, *Energy and fuels*, 26, (2012) 5186.
8. A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, *Carbon*, 43, (2005) 1731.
9. T. Jawhari, Roid A, Casado J. *Carbon*, 33, (1995) 1561. Robertson J. *Adv Phys.* 35 (1986), 317.
10. Adarsh Kaniyoor, Sundra Ramaprabhu, *AIP Advances*, 2, (2012) 032183.
11. A. Ilyin, N. Guseinon, A. Niktin, I. Tsyganov. *Physica E.* 42(8), (2010) 2078
12. Takagi H, Maruyama K, Yoshizawa N, Yamada Y, Sato Y. *Fuel*, 83, (2004) 2427.
13. F. Tuinstra, J. L. Koenig, *J Chem Phys*, 53, (1970) 1126.
14. D. S. Knight, W. B. White, *J. Mater Res*, 4, (1989) 385.
15. CNR Rao, AK Sood, KS Subrahmanyam, A. Govindaraj, *Angew. Chem. Int. Ed.* 48, (2009) 7752.
16. B. Dippel, H. Jander, J. Heintzenberg. *Phys Chem Chem Phys*, 1, (1999) 4707.