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Carbon Nanonecklaces with Carbon Nanotubes and Carbon Dots

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Abstract

Carbon nanoparticles (CNP) have gained significant attention representing unique carbon-based nanomaterials that find applications in various fields of science and technology. Carbon nanotubes (CNTs) and carbon dots (CDs) have now been widely employed as an electrode in super capacitors, as fluorescent nanomaterials for imaging and for fuel cell applications. In the present work, we describe a simple, low cost and chemical free method of synthesizing stable CNPs aligned in the form of a chain popularly known as carbon necklace with CNTs and CDs. Carbon nanoparticles are synthesized by controlled combustion of camphor in a single step flame process. The CNPs synthesized are characterized using X-ray Powder diffraction (XRD), Raman Spectroscopy, Energy Dispersive X ray diffraction (EDX), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible absorption and Photoluminescent (PL) Spectroscopy. The morphology and size of the CNPs are examined using Field Emission Scanning Electron Microscope (FESEM) which shows 'necklace' structure. The CNPs are collected at two different heights and the particles formed are found in the range 30 to 60 nm. The UV- Visible and PL Spectra of the CNPs obtained show the presence CDs. The Raman Spectroscopic and XRD analysis indicate the presence of CNTs in the sample.

Keywords: Carbon nanoparticles, Combustion, Carbon nanotubes, Carbon dots, Carbon necklaces

1. INTRODUCTION

Carbon nanoparticles have gained significant attention in the 21st century being a promising material due to its good electrical/thermal conductivity and enhanced chemical/biocompatibility. It has a wide range of applications in optoelectronics, biological studies, chemical sensing, etc. The important issues with the production of carbon nanoparticles are its cost and quality. There are several chemical and physical methods of synthesizing carbon nanoparticles. Some of them include laser irradiation and exfoliation, sonication, thermal carbonization, etc. One of the important factors in controlling the morphology and the yield of the carbon nanoparticles is the raw materials used in the synthesis. Due to increasing demand for carbon-based nanomaterials in various fields, there is a need to produce carbon nanoparticles of good quality from various carbon sources. In this paper, we introduce camphor as a carbon source for CNPs that can be used in many applications.

The medicinal use of camphor ($C_{10}H_{16}O$) has been documented since ancient times in Asia as well as in Europe. The literature reports the use of various carbon related materials, such as carbon beads, fullerene, diamond-like carbon, glassy carbon, carbon fibers etc., formed from the combustion of camphor using CVD. They find applications in photovoltaic cells, secondary lithium batteries [1-5] etc. Fluorescent CNPs due to their biocompatibility and chemically inert properties have been widely explored in biological labeling, bio-imaging and optoelectronic devices [6-7].

2. EXPERIMENTAL DETAILS

For the synthesis of CNPs Camphor tablets (15 x 7 x 3 mm) are used. Controlled combustion of camphor is carried out by keeping the sample in a silica crucible placed inside a cylindrical pipe with perforations at the bottom. The camphor flame in the luminous yellow zone, known as the carbon zone, is composed of carbonaceous soot particles. The glass plate used to collect carbon nanoparticles from camphor is cleaned with acetone and dried. The soot particles are collected on a glass substrate placed at two different heights of 30 cm and 60 cm. It is observed that the height of the glass plate from the flame and the time duration of deposition play a significant role in getting least agglomerated good nanoparticles. By varying the number of perforations at the bottom of the pipe, the airflow can be controlled. The collected soot is purified by liquid phase oxidation method using a mixture of concentrated sulphuric acid and nitric acid. Then it is quenched with ice cooled water and base neutralized by sodium hydroxide [8].

3. CHARACTERIZATION TECHNIQUES

The morphological characterization and composition study (EDX) of the sample are carried out in Nova Nano FESEM. XRD measurements are done in Bruker D8 Advanced Diffractometer with CuKα radiation (λ=1.5406 Å). FTIR is recorded using Shimadzu IR Prestige-21 and Raman spectrum using Lab Ram Micro-Raman Spectrometer with Argon ion laser (at 514.5 nm wavelength and power of 5 mW) as the excitation source. UV-Visible spectrum is recorded using Jasco V 550 UV-Visible spectrophotometer and Photoluminescent Spectrum of the sample is recorded using Horiba Fluoromax.

4. RESULTS AND DISCUSSION

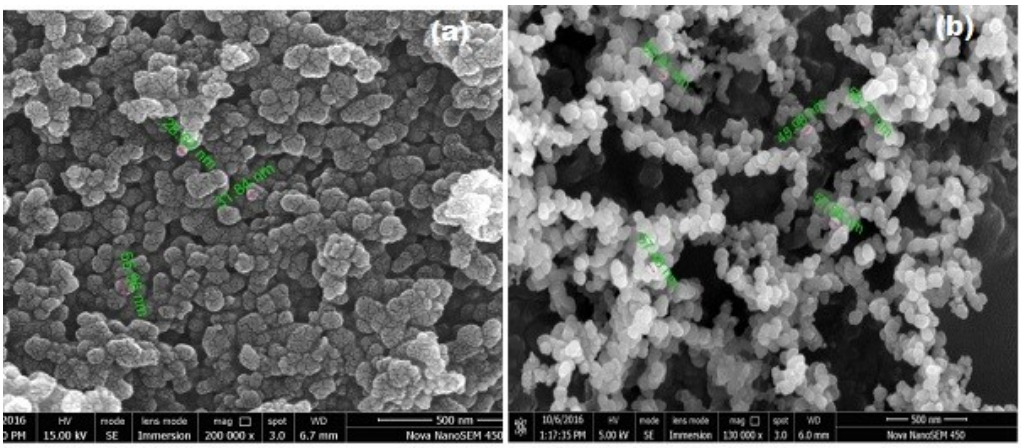

Fig. 1 FESEM image of CNP collected at height (a) 30 cm (b) 60 cm

The carbon particles collected on the glass plate are analyzed using FESEM. Figure 1 (a) show the SEM image of CNPs collected when the glass plate is kept at a height of 30 cm. Agglomerated spherical nanosized carbon particles can be seen in the image. The figure 1 (b) shows the SEM image of CNPs with well-defined boundaries arranged in the form of a chain called carbon necklace when the height at which sample is collected is 60 cm. The particles can be distinguished more clearly in figure 1 (b) when compared with figure 1 (a). The chain of nanospheres is said to be connected by weak Vander Waals force of interactions. The particles formed are of size 30 - 60 nm. Therefore, height is an important factor that decides the morphology and particle size of CNPs formed by combustion method.

FTIR (Fourier Transform Infrared) spectroscopy is an important tool in material analysis which helps in the material identification. The FTIR transmission spectrum of the CNPs is shown in figure 2 (a).

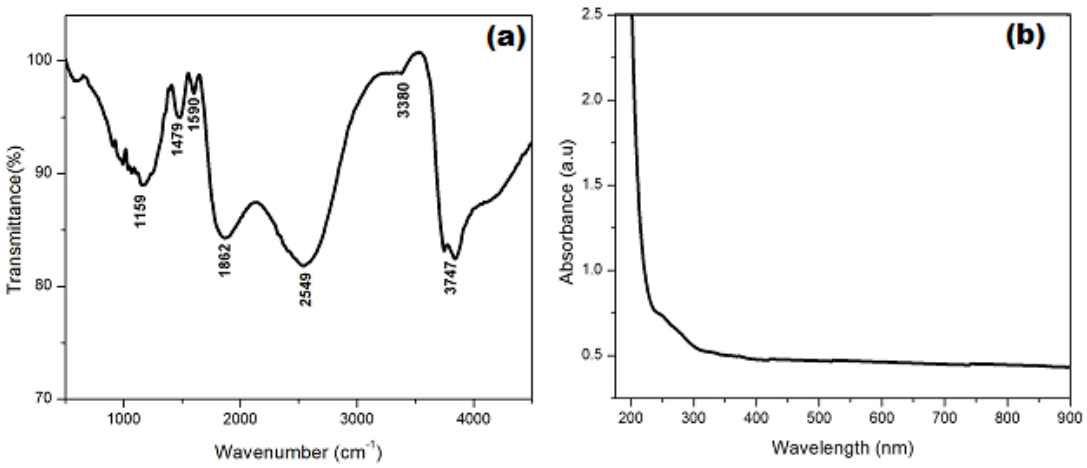

Fig. 2 (**a**) FTIR spectrum of CNPs (**b**) UV- Visible spectrum of CNPs

FTIR spectroscopic analysis is carried out to identify the chemical structure and the presence of any functional group in carbon nanoparticles synthesized. The various bands and their possible vibration modes are given in Table. 1. The presence of the band at 1159 cm^{-1} indicates the presence of sp^2 and sp^3 clusters. The camphor on oxidation undergoes carbonization which gives rise to carbonyl and hydroxyl groups in the spectra. Also, some weak C-H and CH_2 bending vibrations are also obtained.

Table 1.Various modes of vibration in FTIR Spectra

Wavelength(cm^{-1})	**Possible Vibration modes**
3747	alcohol free O-H stretching bands
3380	-O-H hydroxyl groups
2549	C–H bending
1862	C=O stretching bands
1590	-C=C- symmetric stretching
1479	Weak bending of CH_2 absorption
1159	-C-O Carbonyl groups

UV-Visible spectroscopy provides a mechanism to monitor how the nanoparticles change over time. The carbon nanoparticles obtained from the incomplete combustion of camphor are characterized by UV-Visible spectroscopy. The UV-Visible absorption spectrum is shown in figure 2 (b). A broad spectrum is obtained corresponding to the $\pi \rightarrow \pi^*$ transitions of C-C and C=C bonds in sp^2 hybrid regions of the carbon core. Similar broad spectrum is reported [9] to be observed by Carbon Dots due to their complicated band structure and energy levels. The camphor soot sample also gives broad absorption spectra revealing the presence of carbon dots.

The process in which the absorption of light at a particular frequency results in the emission of light due to the excitation – deexcitation phenomena is called photoluminescence. The Photoluminescent Spectra of the CNPs are recorded for three different excitation wavelengths 350 nm, 390 nm, and 430 nm. The corresponding emission spectra are obtained in the range 400 - 500 nm and are shown in figure 3. The maximum emission wavelength is obtained at 426 nm for the excitation at 350 nm. As the excitation wavelength is increased from 350 to 430 nm, the emission wavelength is shifted to longer wavelength regions. For the sample containing quantum dots excitation dependent, PL spectra exhibit a redshift [10]. A decrease in intensity can also be noted from the PL spectra at different excitation wavelengths. It can be attributed to the less number of particles engaged in the electron-hole recombination phenomenon from conduction band bottom to nearby localized electronic states to the valence band top region.

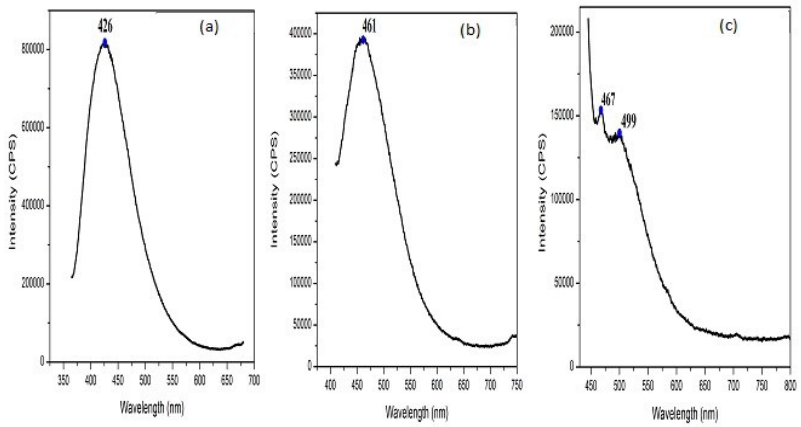

Fig. 3 PL Spectra (**a**) λ_{ex} =350 nm (**b**) λ_{ex}=390 nm (**c**) λ_{ex}=430 nm

The X- ray powder diffraction pattern recorded from the sample under study is found to exhibit 2 prominent peaks (2Θ) at 24.6° and 42.5°, which is in agreement with the reported values. The XRD pattern obtained is shown in figure 4 (a). These peaks denote the presence of multiwalled graphitic carbon nanotubes. The lattice planes corresponding to 24.6° and 42.5° are (002) and (101) respectively [11].

The different forms of carbon such as amorphous, crystalline and nanocrystalline can be characterized by Raman Spectroscopic analysis. The two bands centered around 1368 cm^{-1} and 1594 cm^{-1} are obtained from the Raman spectra of CNPs in the sample as shown in figure 4 (b). The source, camphor is rich in sp^2 and sp^3 hybridized carbon atoms. Only a limited number of phonon modes are Raman active, namely E_{2g} mode for graphite and E_1 and E_2 symmetry modes for CNTs. The density of defects arising in the sample can be found out by measuring the ratio of intensities of D band and G band (I_D/I_G). The study of the D and G bands using Raman spectroscopy gives information about the crystal structure and physical properties of the material.

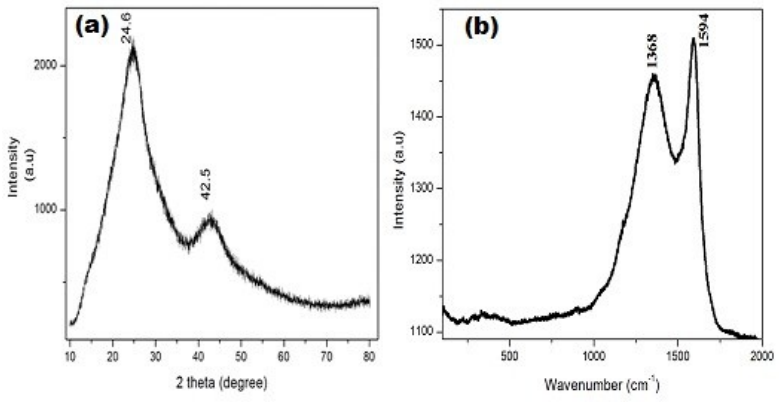

Fig. 4 (**a**) XRD pattern of CNPs (**b**) Raman Spectrum of CNPs

The presence of G band is attributed to the nanocrystalline graphitic structure and D band is observed for amorphous carbon as well as surface defects in CNTs. The I_D/I_G ratio is found to be 0.91 and the crystallite size calculated using the relation by Knight and White is obtained as 20 nm [12]. This confirms the presence of CNTs in the sample.

5. CONCLUSION

The FESEM image of the CNPs prepared in the form of carbon necklace reveal that the particles formed are of the size less than 60 nm. The FTIR spectrum shows several bands corresponding to the possible vibrational modes. Bands denoting C=O, C-O, CH_2, CH_3, OH groups can be clearly seen. The spectrum obtained here shows some similar peaks to that of carbon dots. The broad UV – Visible absorption spectrum tells the presence of carbon dots in the sample. The CNPs formed from camphor exhibit strong fluorescence on excitation with 350 nm. The Excitation-dependent PL spectra give the indication of the presence of carbon quantum dots in the sample. The XRD analysis points the presence of multiwalled graphitic CNTs. Raman spectroscopic analysis revealed the presence of CNTs of crystallite size 20 nm. The D and G band

corresponds to the surface defects in CNTs and multiwalled graphitic structures of carbon nanoparticles.

Thus, the study reveals that the carbon nanoparticle synthesized from camphor by controlled combustion method contains carbon nano-necklaces with carbon nanotubes and carbon dots that find potential application in fuel cell and nanocapacitors. The procedure is simple, cost effective and eco-friendly for CNP, CNT and CD synthesis.

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