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Economical, Green Synthesis of Fluorescent Carbon Quantum Dots from Lac Extract

Amita Jivani[1], Meet A. Moradiya[2]
[1]*University of Science, Department of Chemistry, Gujarat University, Ahmadabad, Gujarat, India*
[2]*School of Nanotechnology, Rajiv Gandhi Proudhyogiki Vishwavidhyalaya, Bhopal, Madhya Pradesh, India*
[2]*Corresponding Author: meetmoradiya2812@gmail.com*

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Abstract: *Fluorescent carbon quantum dots (FCDs) have attracted tremendous interest because of their advantageous characteristics of cost effectiveness and fluorescent nature. In this study, we developed a simple, economical and effective method for the green synthesis of fluorescent carbon quantum dots (FCDs) from Lac of Butea monosperma host tree, a renewable and sustainable resource. The synthesis method involves the low cost hydrothermal process using the Lac extract as a carbon source. The as-synthesized FCDs were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Spectrofluorophotometer. The synthesized FCDs possess stable good water solubility as well as high quantum yield. The results suggest that the proposed FCDs could be utilized for photovoltaic cell, bio imaging, drug delivery and bio-sensor applications.*

Keywords*: Green Synthesis, Fluorescent Carbon Quantum Dots, Lac Extract, Hydrothermal Process*

I. Introduction

Fluorescent carbon quantum dots (FCDs) were first discovered during the study on single-walled carbon nanotubes in 2006 [1], they have attracted lot of attention because of their excellent optical properties and potential applications resulting from the quantum confinement effects [2]. FCDs fascinating class of recently discovered nanocarbons with a size below 10 nm and have attracted considerable research interest due to their excellent photoluminescence, favorable biocompatibility, low toxicity, absence of metals and good water solubility [3]. As a consequence of their outstanding properties, carbon dots form variety of applications in biosensors [4], bioimaging [5], elemental sensors [6] and drug delivery [7] as well as also in catalysis [8] have been demonstrated. FCDs have been synthesized by various methods, including laser ablation [9], electrochemical method [10], hydrothermal method [11], microwave and ultrasonication method [12,13], oxidation of candle soot [5], wet chemical method [6], microwave mediated synthesis [14] and arc discharge [15]. Among them, hydrothermal method was carried out mainly for the synthesis of FCDs from solid waste as a natural precursor. Nowadays, many researchers have been synthesizing FCDs from the natural precursor by using various synthesis routes. Jing Yu et al. developed a green and low-cost hydrothermal method for preparation of water-soluble fluorescent carbon dots, utilizing Jinhua bergamot as a carbon source [16]. Xu Yue et al. demonstrated the fluorescent carbon dots with blue fluorescence were prepared by one-pot hydrothermal treatment in which apple juice was used as raw material [17]. De and Karak et al. reported the fluorescent carbon quantum dots were synthesized by heating process; utilized by banana juice, further he reported the size of as-prepared carbon dots was average 3 nm [18]. Ankit Tyagi and his partners showedwater soluble carbon quantum dots were synthesized from lemon peel waste using a facile and cost effective hydrothermal process, as synthesized carbon dots were 1-3 nm in size with spherical morphology and oxygen rich surface functionalities [19].Himaja et al demonstrated the fluorescent carbon dots were synthesized by refluxing process, in which the Cucumber/Pineapple (Kitchen waste) used as a carbon source [20].

In this work, a green, economical and low-cost hydrothermal method was developed for preparation of water-soluble FCDs with Lac extract as a carbon source. Butea monosperma tree is very promising host tree of kusmi strain Lac insect Kerria lacca. Lac is a resin secreted by the female Lac bug on trees is processed and sold as dry flakes. Thousands of lac insects colonize the branches of the host trees and secrete the resinous pigment. The coated branches of the host trees are cut and harvested as sticklac. The harvested sticklac is crushed and sieved to remove impurities. The sieved material is then repeatedly washed to remove insect parts and other soluble material. The resulting product is known as seedlac. The as-synthesized FCDs possess stable good water solubility and as well as high quantum yield.

II. Material And Methods

Carbon dots were synthesized through greener synthetic route. Initially, 5 g seedlac were washed with water and dried initially in sunlight and then in oven at 100 ˚C for 10 h. h. The dried seedlac were crushed, and then 1 gm crushed seedlac was mixed with 15 mL of water. Afterward the mixture was transferred into a 25 mL Teflon-lined autoclave and heated at 200 °C for a period of 12 h. The large particles were removed from the product by filtration with a 0.22 μm filter membrane and then centrifuged at 15000 rpm for 15 min and finally dried under vacuum for 48 h. The carbon particles were dispersed in distilled water at a concentration of 0.5 mg/mL for further characterization and use.

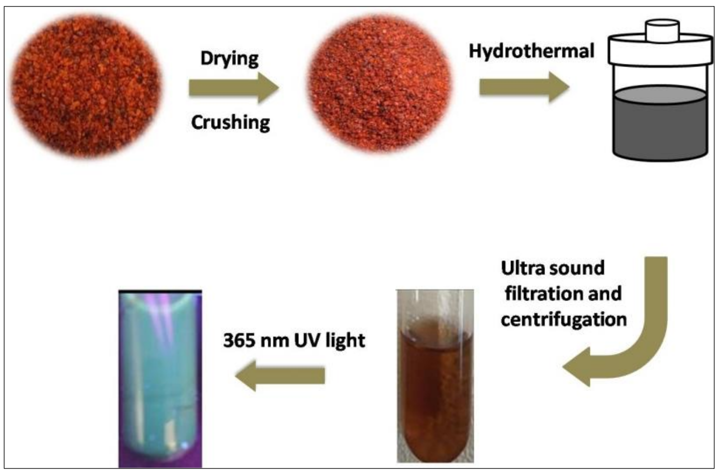

Figure 1: Illustration of fluorescent carbon quantum dots synthesis.

Characterization

The synthesized of FCDs from seedlac was characterized by using various spectroscopic and microscopic studies. The crystallinity and phase purity of the synthesized FCDs was analyzed by using X-ray diffraction (XRD) analysisX-ray pattern equipped with Cu Kα radiation (λ=1.5406 Å) with the targeted voltage of 45 kV. The morphological image of FCDs was obtained by transmission electron microscope (TEM) using an acceleration voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. The UV-visible absorption spectrum of FCDs was recorded using spectrophotometer.The fluorescence spectrum was recorded with single beam Spectrofluorophotometer. The sample was recorded in different excitation wavelength (λex= 300 to 540 nm).

Quantum yield measurements

The quantum yield of the carbon dots was determined at an excitation wavelength of 360 nm by the equation [21]

$$Q_{CD} = Q_R \frac{I_{CD}}{I_R} \cdot \frac{A_R}{A_{CD}} \cdot \frac{\eta_{CD}^2}{\eta_R^2}$$

(1)

where ‘Q’ is the quantum yield, ‘I’ is the intensity of luminescent spectra, ‘A’ is the absorbance at exited wavelength and ‘g’ is the refractive index of the solvent used; using quinine sulfate (quantum yield 54%) in 0.1 M H_2SO_4 solution as the reference. The subscripts ‘CD’ for carbon dots and ‘R’ for reference are used in this equation.

III. Results and Discussion

Structural and Morphological Analysis of FCDs

The result of the XRD measurement of the synthesized FCDs is shown in figure 2. The XRD characteristics peaks are appeared at 2Ɵ = 20.6°, 22.8°, 42.3°and 45.7°. The major peak of the FCDs was appeared at 20.6 ° and 42.3 °. This is due to the presence of graphitic carbon [13]. A very intense peak was observed at 20.6° corresponding to (311) plane of carbon. The weak peak observed at 42.3° is assigned to the plane of (533). This diffraction pattern completely matches with carbon corresponds to the JCPDS value of (82-0505) and hence the FCDs is a face centered cubic crystals.

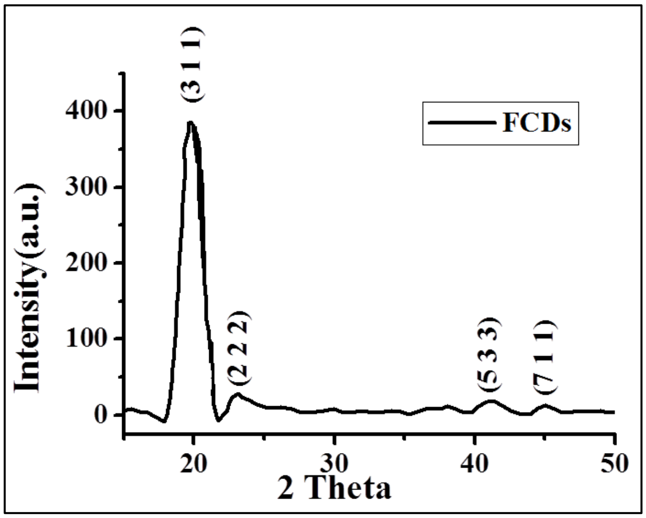

Figure 2: XRD spectrum of as-prepared carbon quantum dots

Figure 3 shows a TEM image of the products thus formed, revealing that they consist of nanoparticles well separated from each other. The TEM image clearly indicates that the FCDs are smaller in size and nearly spherical in shape. The average size of the synthesized FCDs was found to be 3-4 nm. The high-resolution TEM (HRTEM) image taken from one nanoparticle (inset in Figure 3) shows a crystalline structure with lattice spacing of 0.20 nm. The lattice spacing of 0.20 nm matches well with the (102) lattice spacing of graphite, which is quite similar to previous reports on FCDs [22, 23].

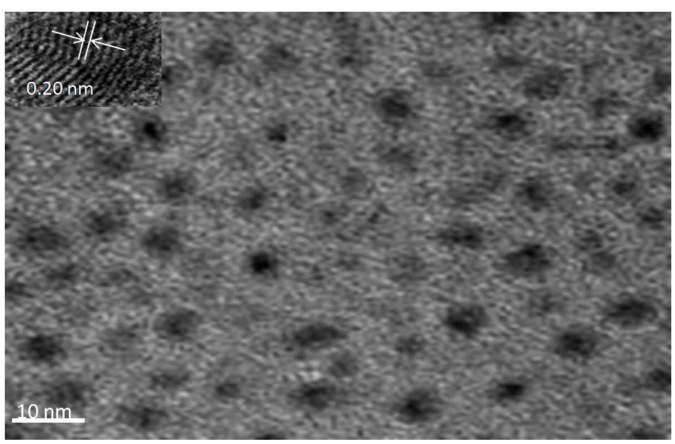

Figure 3: TEM images of the products thus formed. The inset shows the HRTEM image of one quantum dot.

Optical Properties of FCDs

The fluorescence intensity is also dependent on the excitation wavelength. The maximum excitation and emission wavelengths of the FCDs aqueous solution are 350 and 420 nm, and with increasing the excitation wavelength (300 nm to 540 nm with 20 nm increment as shown in figure 4(b)). The FCDs suspension exhibits a bright blue fluorescence under 360 nm UV light.

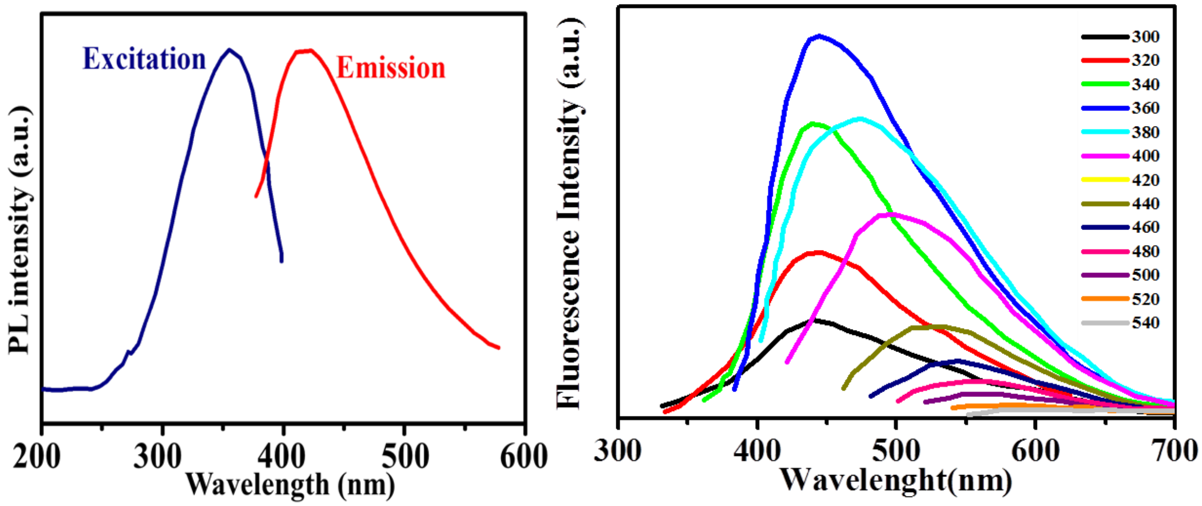

Figure 4: (a) The excitation (blue line) and emission (red line) spectra of the obtained FCDs; (b) photoluminescence (PL) emission spectra of the FCDs at various excitation wavelengths from 300 nm to 540 nm (with 20 nm increment).

The emission peak was also shifted to a higher wavelength with the increase of the excitation wavelength, which is shown clearly in Fig. 4(b). The difference in the position of emission peak is due to the variation in size of the carbon dots. The energy gap increases with the decrease in size of the carbon dots and vice versa due to the quantum confinement effect like semiconductor quantum dots. Thus the particles with a smaller size get excited at a lower wavelength, whereas those with a larger size get excited at higher wavelengths [18]. The intensity of the photoluminescence (PL) depends on the number of particles excited at a particular wavelength. The highest photoluminescence intensity of carbon dots was observed at an excitation wavelength of 360 nm, because of the largest number of particles being excited at that wavelength. Another reason for the excitation dependent PL behavior of carbon dots is the nature of their surface. The presence of various functional groups on the surface of the carbon dots may result in a series of emissive traps between π and π* of C–C. On illuminating the carbon dots at a certain excitation wavelength a surface energy trap dominates the emission [24]. The use of quinine sulfate as a reference quantum yield of carbon dots in aqueous solution as measured at an excitation wavelength of 360 nm and was found to be 8.9 %. Thus the characteristic PL of the prepared carbon dots is promising for their different possible applications. The results suggest that the current FCDs could be a good alternative to photocatalysis, drug delivery, bio-imaging and bio-sensor applications.

IV. Conclusion

In this study, we have demonstrated facile, simple and cost effective hydrothermal synthesis of water soluble fluorescent carbon quantum dots, using seedlac. The hydrothermal synthesis has the merits of green synthesis and resource-saving process with short reaction time.The XRD peak of synthesized FCDs indicates the face centred cubic crystal structures. The TEM studies indicate the crystalline nature of the FCDs with a size of 3-4 nm. It showed broad excitation and emission spectrum and excitation wavelength with high quantum yield approximately 8.9 %. The highly crystalline and fluorescent FCDs provide good potential for bio-sensors, bio-medical, imaging, drug delivery and solar cell applications.

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The authors declare that they have no known competing financial interests.

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