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The Synthesis of Highly Fluorescent Carbon Quantum Dots from Tartaric Acid

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Abstract: Carbon quantum dots (C-dots) 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 using low-cost hydrothermal treatment of Tartaric acid as a carbon source. The as-synthesized C-dots were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV–Vis absorption spectroscopy, Spectrofluorophotometry, Fourier transform infrared spectroscopy (FT-IR). The synthesized C-dots possess stable fluorescent properties, good, bio-compatibility, and high quantum yield. The C-dots are highly crystalline, with longitudinal dimensions of 3.128 ± 0.17 nm. The XRD and TEM analysis indicates that the synthesized C-dots have a nearly spherical morphology and narrow size distribution. The results suggest that the proposed C-dots could be utilized for photovoltaic cell, bioimaging, drug delivery, and biosensor applications.

Keywords: Green Synthesis; Carbon quantum dots; Tartaric acid; Hydrothermal process.

1. Introduction

Carbon quantum dots were first discovered during the study on single-walled carbon nanotubes in 2006 [1], they have attracted a great deal of attention from the researchers due to their unique properties such as, low cost and facile synthesis, chemical stability, favorable biocompatibility, excellent photoluminescence, absence of metals, low-toxicity, and good water solubility [2]. Carbon dots are of much interest compared to traditional quantum dots, as they are produced using carbonization of glucose, sucrose, glycerol, citric acid, ascorbic acid, etc. [3]. As a consequence of their outstanding properties, carbon dots form a variety of applications in biosensors [4], bioimaging [5], elemental sensors, [6], and drug delivery [7] and demonstrated in catalysis [8] as well. C-dots 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]. There are two main methods for preparing carbon quantum dots. One is prepared using large carbon materials, such as carbon fibers, graphite powder, or graphene, and the other is by physically or chemically treated organic compounds such as polyethylene glycol, citric acid, sucrose, glucose and chitosan [16-18]. Comprised with the method using large carbon material, The chemically treated organic have advantages of inexpensive and biocompatible raw materials, relatively green and mild synthetic routes, and no special precision instruments are required [19]. Carbon

dots prepared by organic compounds have rich hydroxyl, carboxyl, and epoxy groups that stabilize the energy traped on the surface of the carbon dots and cause the fluorescence emission of carbon dots. Du et al. provided the 19.2% QY of C-QDs obtained by the hydrothermal treatment of citric acid and 2-(2-aminoethoxy)-ethanol [20]. Zeng et al. reported that fluorescence C-QDs with 43.8% QY for sensitive and selective detection of iodide [21]. Although the mechanism for the fluorescence of carbon dots is still unclear, the hypotheses of emission defects and electron conjugate structures are two explanations for it [22]. Thus, researches on the synthesis of fluorescence carbon dots using organic compounds have attracted much attention in recent year.

In this paper, phenylalanine associated with Tartaric acid were used as carbon sources for the synthesis of fluorescent carbon dots. The method is a facile, economic, and one-step hydrothermal method, and the prepared fluorescence carbon dots are expected to exhibit strong blue light emission of around 440 nm. We characterized the structure of the as-prepared C-dots and studied the fluorescence property of CDs.

2. Materials and Methods

The carbon dots (CDs) were synthesized via a simple hydrothermal method. In a typical synthesis, tartaric acid (2 gm) and aniline (1 gm) were sufficiently dissolved in 25.0 mL of ultrapure water, and then the solution was heated at 170 °C for 24 h in a 50.0 mL Teflon lined. After that obtained yellow product was placed in a dialysis bag (M_w = 3500 Da) to remove the unreacted reagents. When CDs were used for detection, the concentration of the original solution was calculated using the concentration of urea. In order to meet the needs of characterization, we have to solidify this solution for which we have dried in a vacuum oven at 70 °C for 3 days to obtain the solid powder product which was placed in a refrigerator at 4 °C. The synthesized C-dots were characterized by using various spectroscopic and microscopic studies. The crystallinity and phase purity of the synthesized C-dots was analyzed by using X-ray diffraction (XRD) that equipped with Cu Kα radiation (λ=1.5406 Å) with the targeted voltage of 45 kV. The morphological image of C-dots was obtained by a 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 a carbon-coated copper grid and dried at room temperature. The UV-visible absorption spectrum of C-dots was recorded using a spectrophotometer. The fluorescence spectrum was recorded with a single beam Spectrofluorophotometer. The sample was recorded in different excitation wavelengths (λex= 300 to 540 nm).

The quantum yield of the carbon dots was determined at an excitation wavelength of 360 nm by the equation [23]

$$Q_{CD} = Q_R \frac{I_{CD}}{I_R} \cdot \frac{A_R}{A_{CD}} \cdot \frac{\eta_{CD}^2}{\eta_R^2} \quad (1)$$

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

3. Results and Discussion

The result of the XRD measurement of the synthesized C-dots is shown in figure 1(a). The XRD patterns show a broad and intense diffraction peak centered at 2θ=23° and a weak peak at 2θ=41° which are assigned to (002) and (101) diffraction pattern of graphitic carbon as shown in Fig 1a which indicates the amorphous nature of the C-dots and is in accordance with previous structure analysis on disordered amorphous graphitic carbon quantum dots [24].

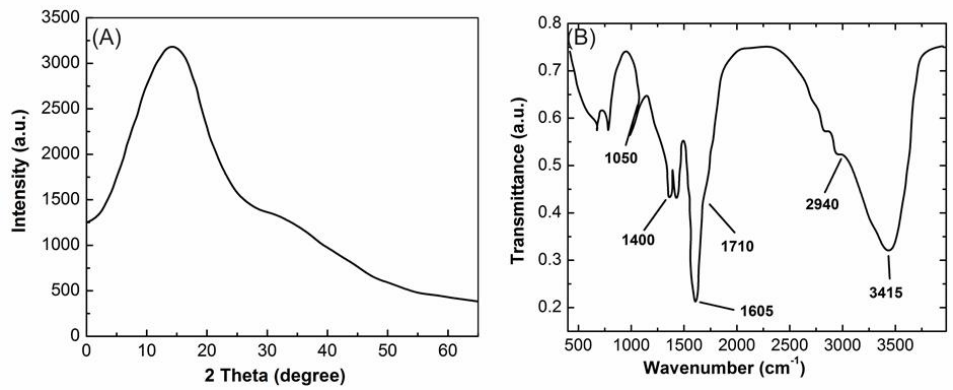

Figure 1. (a) XRD spectrum of as-prepared C-dots. (b) FTIR spectra of as-synthesized C-dots.

FTIR analysis was performed to analyze the presence of polar functional groups over the C-dots surface. The characteristic absorption bands for –COOH and –OH groups are observed, as shown in Fig. 2 (b). Broadband at ~ 3414 cm-1 appears for the −OH stretching frequency. The peak at 1605 cm-1 and 1405 cm-1 is a signature for the existence of -COO^-. The peak of 1715 is due to the existence of C=O. A C-H vibration peak appears at 2940 cm-1. FTIR spectrum reveals the presence of hydrophilic surface functional groups over the C-dots surface, imparting the excellent water solubility. The TEM image of the product is snown in Figure 2(a). The TEM image indicates that the well separated, nearly spherical, and smaller in size C-dots are obtained. The average size of the synthesized C-dots is found to be 3.128 nm.

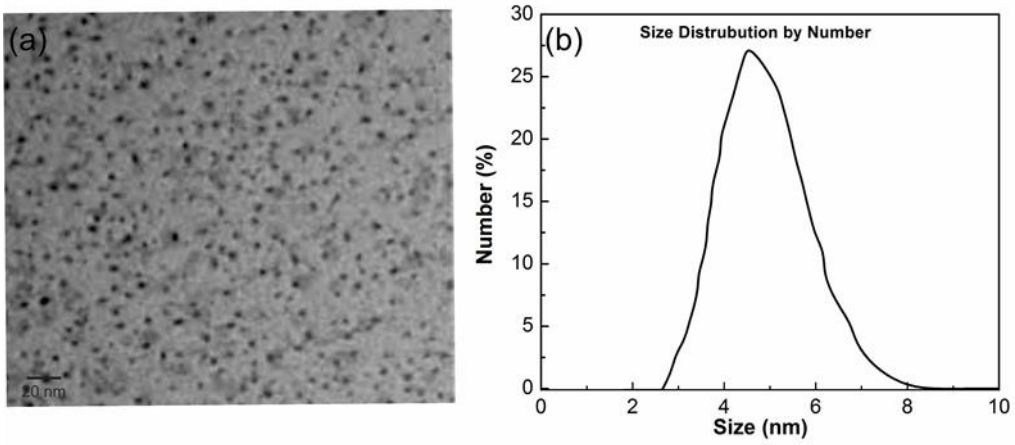

Figure 2. (a) TEM image of as-synthesized C-dots. (b) Size distribution graph of C-dots.

The fluorescence intensity is also dependent on the excitation wavelength. The maximum excitation and emission wavelengths of the C-dots aqueous solution are 360 and 450 nm, and with increasing the excitation wavelength (300 nm to 540 nm with 20 nm increment as shown in figure 3(b)). The C-dots suspension exhibits a bright blue fluorescence under 360 nm UV light.

To evaluate the optical properties of the synthesized C-dots, UV–Vis absorption and fluorescence excitation and emission spectra were measured. The synthesized C-dots have two absorption peaks at 240 and 350 nm (Fig 3(a), black line), which are probably assigned to the typical absorption of aromatic π – π* systems and the n – π* transition of C-dots respectively [25]. The brown aqueous solution of C-dots appears brilliant blue under UV irradiation (Fig 3a and b), confirming the bright photoluminescence of the prepared C-dots. To describe the photoluminescence of C-dots, excitation and emission spectra were recorded using a spectrofluorometer and maximum excitation intensity obtained at a wavelength of 365 nm (Fig 3(a), red line) while maximum emission intensity obtained at a wavelength of 450 nm (Fig 3(a), green line). To address whether the synthesized C-dots showed excitation dependent photoluminescence or not, different emission spectra upon varying excitation wavelengths were recorded.

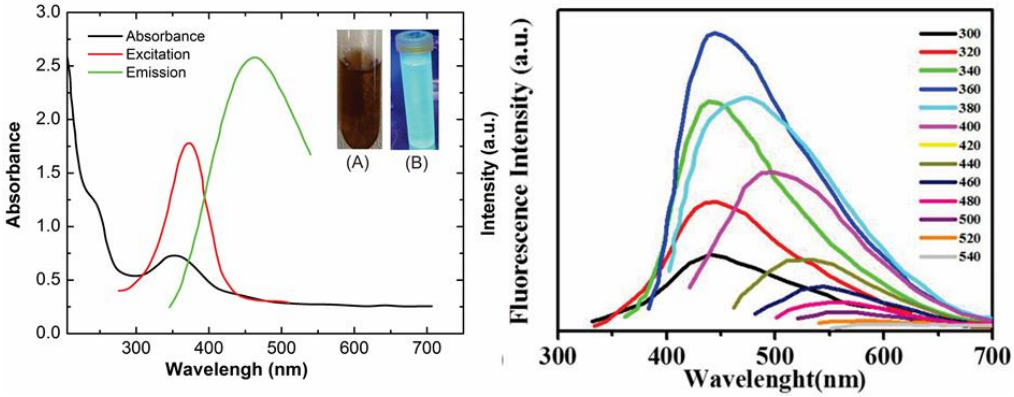

Figure 3. (a) The absorption (black line), the excitation (red line) and emission (green line) spectra of the obtained C-dots; (b) photoluminescence (PL) emission spectra of the C-dots at various excitation wavelengths from 300 nm to 540 nm (with 20 nm increment).

Fig 3(b) demonstrates the photoluminescence emission spectra of the C-dots with excitation wavelengths ranges from 300 nm to 540 nm. The fluorescence graph of the sample possesses the symmetrical emission peaks and increased excitation wavelengths.

To address whether the synthesized C-dots showed excitation dependent photoluminescence or not, different emission spectra upon varying excitation wavelengths were recorded. Fig 3(b) demonstrates the photoluminescence emission spectra of the C-dots showing excitation wavelengths from 300 nm to 540 nm. Emission spectra, presented in Fig. 3 (b) clearly reveals the tunable emissive nature of C-dots. The increase in excitation wavelengths causes redshift on emission wavelengths, which is recognized as a generic feature of carbon core [26]. These tunable emissions depicted the multicolor behavior of C-dots. The emission intensity increases from λ_{ex} 300 nm to 360 nm then gradually decreases up to λ_{ex} 540 nm. The highest emission intensity was observed for excitation at 360 nm. Hence, λ_{ex} of 360 nm was selected. Thus the characteristic PL of the prepared carbon dots is promising for their different possible applications. The results suggest that the current C-dots propose a potential alternative to photocatalysis, drug delivery, bio-imaging, and bio-sensor applications.

4. Conclusions

In this study, we have used tartaric acid and aniline as a carbon source and demonstrated a facile, simple, and cost-effective hydrothermal method for the synthesis of water-soluble fluorescent carbon quantum dots. The methodology adopted here can be considered as a green

synthesis process having an advantage of short reaction time and resource-saving. The as-synthesized C-dots have a nearly spherical morphology and narrow size distribution. It showed a broad excitation and emission spectrum. The excitation wavelength with a high quantum yield of approximately 8.9 % is obtained. The highly crystalline and fluorescent C-dots synthesized in this study offer good potential for bio-sensors, bio-medical, imaging, drug delivery, and solar cell applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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