Research Article

Green Synthesis of Carbon Dots from Grapefruit and Its Fluorescence Enhancement

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In this study, undoped carbon quantum dots (UCQDs, UCQDs-peel) and N-doped carbon dots (NCQDs) were prepared by a facile one-pot environmentally friendly hydrothermal method using grapefruit as carbon sources in the absence and presence of area, respectively. The structure, morphology, and fluorescence properties of three samples were characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and photoluminescence (PL). It was found that three types of CQDs could emit blue fluorescence with different intensities when irradiated with ultraviolet light. Compared to the luminescence properties of UCQDs, NCQDs, and UCQDs-peel, it can be seen that the fluorescence intensity of NCQDs was strongest due to the presence of NH and C-N bonds.

1. Introduction

Carbon quantum dots (CQDs) have widespread application in light-emitting devices (LED), cancer therapy, thermometers, anticounterfeiting, and biosensors due to their unique and tunable optical properties, the low cost and environmentally friendly fabrication, and low cytotoxicity and a high resistance to photobleaching [1–5]. Recently, lots of researchers have been working on CQDs from the preparation to application, especially in green synthesis from some natural sources such as grass [6], leaves [7], flowers [8], cereal [9], and so on [10, 11]. However, in practice applications, CQDs are limited for its low luminescence intensity and single emission wavelength. So, the studies on the development of efficient and reproducible strategies to enhance the intensity and multicolor emission of CQDs would improve their practical applications in sensing, imaging, LED, and so on.

According to studies of the existing luminescence mechanism, the fluorescence intensity of CQDs was influenced by surface states [12] and the structure [13] and size [14] of the materials. So far, scientists have made some researches on the enhancement of fluorescence intensity and tunable multi-

color emissions of CQDs in order to realize its practical application. All in all, there exist several strategies including prepared method [15], surface modification and passivation [16], different solvent [17] and heteroatom doping [18], high pressure [19], and so on [20]. For example, Wang and his coworkers successfully obtained fluorescence enhancement of CQDs via simple grinding, prepared using pyrene derivative (pyrene-1-butylric acid (PyBA)) as a carbon source; furthermore, they found that an apparent 20-30 times emission enhancement can be observed by the treatment of grinding, which was ascribed CQD-packed structure and morphology changes [21]. At the same time, Wang et al.'s team also studied the pressure-triggered aggregation-induced emission enhancement in red emission amorphous CQDs and revealed that the accumulation of R-CQD molecules triggered enhanced emissions under higher pressure by theoretical calculations [22]. Xu et al. reported a novel kind of (AA)-enhanced CQDs prepared based on the employment of green teas and ascorbic acid by adjusting its surface state. Moreover, they found that this new kind of (AA)-enhanced CQDs also reveals excellent antioxidant activity [23]. In addition, many studies have proved that

FIGURE 1: Illustration of the preparation procedures and fluorescence characterization of (a) UCQDs, (b) NCQDs, and (c) UCQDs-peel.

heteroatom like N, S, F, rare earth, and codoping can improve the luminescence performance of CQDs, such as tunable emission and multifunction properties [24, 25]. However, as we all know, there is little research on the fluorescence enhancement of CQDs by N-doping by a one-pot green synthesis method.

In this work, three kinds of carbon quantum dots (CQDs) are prepared using different sets of natural grapefruit and urea materials by a facile one-pot environmentally friendly hydrothermal method. Subsequently, the fluorescence properties of the prepared samples were investigated systematically. It was found that the prepared carbon quantum dots can emit blue fluorescence with different intensities when irradiated with ultraviolet light. Furthermore, the fluorescence intensity of CQDs can be improved by N-doping. Therefore, the method of enhancement fluorescence intensity by heteroatom doping holds a promising potential application in bioimaging, ion sensing, and LED.

2. Materials and Methods

2.1. Experimental Materials and Reagents. The fresh grapefruits were purchased from a local supermarket of Northeast Forestry University, China. Urea was obtained from Tianjin Tianli Chemical Reagents Ltd. Nitric acid was obtained from Xintian Chemical Reagents Ltd. (Shuangcheng, Heilongjiang Province). All of the reagents were of reagent grade and used without any further purification. The deionized water was prepared in the lab.

FIGURE 2: XRD patterns for (a) UCQDs, (b) NCQDs, and (c) UCQDs-peel.

2.2. Apparatus and Procedures. X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/max- γ B diffractometer equipped with a rotating anode and a Cu K α source ($\lambda = 0.154056$ nm). Transmission electron microscopy (TEM) images were obtained on a TecnaiG2 F20 electron microscope (FEI, Holland) with an accelerating voltage of 200 kV. Fourier-transform infrared spectra (FT-IR) were recorded on a Perkin Elmer TV1900 instrument (Waltham, MA, USA). Spectra were recorded from 650 to 4000 cm^{-1} , at a resolution of 4 cm^{-1} . UV-vis absorption spectra were examined by a U-3900 UV/Visible spectrometer (Hitachi Company). The fluorescence spectra were carried out on FluoroMax-4 fluorescence spectrometer.

FIGURE 3: TEM images of (a) UCQDs, (b) NCQDs, and (c) UCQDs-peel. (d)–(f) are the corresponding size distributions obtained from TEM images.

2.3. Preparation of CQDs and NCQDs. Figure 1 is the illustration of preparing three kinds of CQDs, and the process of the synthesizing CQDs is as follows:

After peeling the skin, the grapefruit was cut into small pieces and fresh juice was squeezed out. The obtained juice was centrifuged at 8000 rpm for 10 min; the above supernatant was passed through a filter paper to get pulp-free grapefruit juice. Then, 20 mL filtered grapefruit juice and 20 mL deionized water were mixed under stirring for 15 minutes. The above mixture was transferred into a Teflon-lined steel autoclave and heated at 180°C for 6 h. After the system was cooled to the room temperature, the obtained brown products were centrifuged for 15 min with a speed of 5000 rpm and then the resultant solution was dialyzed in a dialysis bag (MwCO = 3500 D) for 48 h. Finally, the products were freeze-dried for further analysis.

NCQDs were prepared by the same way by using grapefruit juice as the carbon source and carbamide (1 mol/L) as both the carbon and nitrogen source.

CQDs from grapefruit peel were prepared as follows: grapefruit peel was cleaned by the deionized water and then chopped. After that, the chopped grapefruit peel was heated at 220°C in a muffle furnace for 2 h. After cooling down at room temperature, 20 mL deionized water was added into the products and ultrasound stirred for 20 min. The solution was then filtered to remove precipitates and to obtain the CQDs-peel.

3. Results and Discussion

3.1. Structure and Morphology of Prepared Samples. The XRD patterns of three kinds of samples are shown in Figure 2. The

FIGURE 4: Comparison of Fourier transforms infrared spectra of carbon dots prepared by three carbon sources (a) UCQDs, (b) NCQDs, and (c) UCQDs-peel.

obvious broad peak around at 22.4° ($d = 0.396$ nm) were found in three samples of XRD patterns, which indicated highly disordered carbon atoms and graphitic structure of the CQDs. There is no other peak found in Figure 2, indicating three prepared samples were pure amorphous nature of CQDs.

The morphology and size of the prepared samples were measured by TEM. As shown in Figure 3, it was found that three kinds of samples had uniform spherical morphology. The diameter of the UCQDs is larger than those of NCQDs and UCQDs-peel. And their diameters are mainly distributed

FIGURE 5: (a) The fluorescence spectra of UCQDs (a1), NCQDs (b1), and UCQDs-peel (c1), under the different excitation wavelengths. (b) The UV-vis absorption spectra of UCQDs (a2), NCQDs (b2), and UCQDs-peel (c2).

FIGURE 6: The fluorescence spectra of (a) UCQDs, (b) NCQDs and (c) UCQDs-peel with the same fixed concentration. The inset is the photos of solution of CQDs under the irradiation of 365 nm.

in the range of 4.74–8.20 nm with an average diameter of 6.34 nm and a range of 2.45–6.23 nm with maximum population at about 4.44 nm and 3.39 nm, respectively.

3.2. The Analysis of Surface Chemistry Compositions. To investigate the surface chemistry characteristics of the three kinds of CQDs from grapefruit, the prepared samples were characterized by FTIR spectroscopy. As shown in Figure 4, it can be seen that the similar absorption peaks were found in three prepared samples. And the absorption peaks at about 3675 cm^{-1} and 1050 cm^{-1} can be ascribed to the stretching vibration of carboxylic acid ($-\text{COOH}$) and hydroxyl group (O-H) [26]. The peaks at 2976 cm^{-1} and 2900 cm^{-1} corresponded to the vibration mode of C-H. The peaks observed at 1733 , 1572 , and 1388 cm^{-1} corresponded to the stretching vibrations of the C=O, C=C, and C-N groups, respectively. Furthermore, three samples have similar IR bands within the range of $\sim 1000\text{ cm}^{-1}$ which are assigned to the stretching vibrations of C-H. In addition, the peak at 1250 cm^{-1} is observed in UCQDs and UCQDs-peel assigned to armchair configuration, which appears at the edges of graphene layers being consistent with carbene and carbene structures at armchair sites [13]. And the presence at about 3173 , 750 , 1667 , and 1448 cm^{-1} in the NCQDs due to the stretching or bending vibration of the N-H, CONH, and C-N groups [27], which indicates the effective nitrogen doping into CQDs occurring from urea.

3.3. Fluorescence and UV-vis Absorption Spectra. The optical properties of three kinds of obtained samples were investigated by FL emission and UV-vis absorption spectra. Figures 5(a), 5(b), and 5(c) present CQDs, NCQDs, CQDs-1, respectively. It can be found that the three kinds of CQDs show the excitation-dependent emission spectral behavior with different maximum emission wavelengths when the excitation wavelength varied from 300 to 420 nm with an increment of 20 nm. The FL intensity increased gradually and then decreased, and the strong emission peaks were found at 411 nm (Figure 5 a1, ex: 320 nm), 418 nm (Figure 5 b1, ex: 340 nm), and 420 nm (Figure 5 c1, ex: 340 or 360 nm), respectively.

UV-vis absorption spectra of three kinds of CQDs exhibit different absorption bands due to different surface states. Two different absorption bands are found in Figure 5 a2 (for UCQDs), which are ascribed to a typical absorption of an aromatic system. The weak absorption peak at 225 nm can be attributed to the $n-\pi^*$ transition of C=C bonds. The strong peak at 283 nm is assigned to the $\pi-\pi^*$ transition of C=C bonds for aromatic sp^2 hybridisation (shown in Figure 5 a2) [28]. However, multiple absorption peaks were observed in Figure 5 b2 (for the NCQDs). The strong peak at 271 nm can be attributed to the transition of $n-\pi^*$ and $\pi-\pi^*$ with C=O bonds of carboxyl groups and aromatic sp^2 (C=C) domains, respectively [29]. And the absorption bands at about 308 nm, 324 nm, 329 nm, and 334 nm indicate that the surface of the synthesized NCQDs molecules has amide functions. In Figure 5 c2, the broad absorption band from 240 to 280 nm was observed which is contributed to the $\pi-\pi^*$ transition of C=C bonds for aromatic sp^2 hybridisation.

The fluorescence spectra of CQDs from different reactive materials are shown in Figure 6. It was found that CQDs from different reactive materials showed similar fluorescence properties and different fluorescence intensity, when the concentration of CQDs fixed the same. UCQDs and NCQDs had the same fluorescence properties and different fluorescence intensities. In contrast, NCQDs showed a strong luminous intensity being ascribed to N-atom doping in the CQDs, which corresponded to the optical properties of CQDs improved via the edge doping [30]. And the edge doping increased photoexcited electron in the emission transition channel, thereby enhancing the radiation transition probability and the PL intensity [16]. In addition, UCQDs-peel exhibited a red-shifted PL emission in comparison to the UCQDs and NCQDs. According to the above FTIR analysis, three kinds of CQDs are hydrophilic due to the surface polar groups, which are highly dispersible in water, and the solution of CQDs exhibits strong light blue light under the irradiation of 365 nm xenon lamp (shown in the inset of Figure 6).

4. Conclusions

In summary, a green and facile synthesized method was presented to prepare NCQDs with enhanced luminescence intensity by grapefruit juice and urea under hydrothermal treatment. UCQDs, NCQDs, and UCQDs were successfully synthesized by using grapefruit juice, grapefruit juice, and urea and grapefruit peel as reactive materials, respectively. The analysis of structure, composition, and fluorescence properties indicates that nitrogen atom doping can enhance the fluorescence intensity due to the edge doping increasing photoexcited electron in the emission transition channel, thereby enhancing the radiation transition probability and the PL intensity. In addition, UCQDs-peel exhibited a red-shifted PL emission in comparison to the UCQDs and NCQDs, which may be related to the size increase of CQDs.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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