Fluorescence of CQDs Synthesized by Hydrothermal Method

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Abstract. Carbon quantum dots (CQDs) are widely used in biological imaging, biosensors and nanomaterials. Because of their good optical properties, biocompatibility, low toxicity, easy surface functionalization and other advantages. In this paper, Carbon quantum dots was prepared by one-step hydrothermal method with glucose as carbon source. The effects of the reaction time and the reaction temperature were investigated. The morphology of CQDs was observed by transmission electron microscopy and their structural properties were characterized using fluorescence spectrum, Fourier transform infrared spectrum and uv-visible spectrum. The experimental results show that CQDs with good performance is synthesized successfully by this method, and the synthesized CQDs has the best performance at 180℃ and 8 h.

1. Introduction
Carbon quantum dots are a new kind of carbon nanomaterial with sizes less than 10 nm [1-2]. Metal quantum dots contrast, carbon quantum dots not only have the advantages of the macroscopic quantum tunnelling effect, size effect, surface effect [3], but also have good light stability and photobleaching resistance, and a long fluorescence lifetime. They also have excellent optical properties. For example, the absorption spectrum is wider and the emission spectrum is narrower. In addition, most metallic quantum dots contain toxic heavy metals, harmful to the environment, and difficult to apply in living cells [4]. The low toxicity of carbon quantum dots makes it possible to replace metal quantum dots, which are widely used in analytical detection [5], optoelectronic devices, bioimaging and labelling.

CQDs are mainly composed of C, H and O elements. However, due to the different preparation methods for CQDs and the different types of raw materials, different ratios of these elements are obtained in CQDs. In addition, the surface of CQDs contains various oxygen-containing functional groups such as carboxyl groups, hydroxyl groups [6]. Using the reactivity of these groups, CQDs can be combined with other materials to obtain composite materials with improved properties. This approach broadens its application in the fields of detection and sensing [3].

Since the discovery of carbon quantum dots, they have been studied by many domestic and international researchers because of their outstanding physical and chemical properties. After years of development, this research has yielded fruitful results, and many methods have found for preparing CQDs. These preparation methods can be roughly divided into top-down synthesis methods or bottom-up synthesis methods, depending on the raw materials used in the preparation process. Top-down synthesis involves the separation of small-sized CQDs by physical or chemical methods from carbon materials like graphite rods, carbon powder, and activated carbon. Specific top-down synthesis methods include arc discharge [7], laser ablation [8], electrochemical synthesis [9]. Bottom-up
synthesis involves the synthesis of carbon quantum dots using carbon-containing organic small molecules or materials in an ionic state as the carbon source. These methods include hydrothermal synthesis, combustion [10], templating [11], microwave synthesis [12], and ultrasound assisted synthesis [13]. In this paper, carbon quantum dots (CQDs) were prepared via a hydrothermal method using glucose as an environmentally friendly and cheap raw material. The optimal synthesis conditions were determined by changing the reaction temperature and reaction conditions. This research will promote the application of CQDs in optoelectronic devices, analytical detection, bioimaging and labeling.

2. Experimental

2.1. Material Synthesis
The primary reagents were glucose (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}•H\textsubscript{2}O) and sodium hydroxide (NaOH). The reagents used were all analytical grade and the water used was pure water. Preparation of the carbon quantum dots: 1.44 g of glucose was accurately measured on a balance, then dissolved in 25 mL of water. After stirring for 10 minutes at room temperature, the solution was transferred to a homogeneous reactor. The reaction time was from 4 h to 10 h, and 2 h was an interval. The reaction temperature ranges from 160 °C to 220 °C, with an interval of 20 °C. After the reaction was completed, cooled the solution to room temperature to obtain a yellow solution of CQDs. The prepared CQDs were transferred to a pretreated dialysis bag and immersed in deionized water for 24 h. After dialysis, then the CQDs were freeze-dried for 36 h to obtain a solid composed of CQDs. The dialysis bag was pretreated as follows: First, the dialysis bag (1000 Da) was cut into 10-13 cm sections. Then it was boiled in 50% ethanol for 1 hour, and washed sequentially with 50% ethanol and a solution of 0.01 mol L\textsuperscript{-1} sodium bicarbonate and 1 mmol L\textsuperscript{-1} EDTA (pH was 8.0). Finally, it was rinsed with deionized water 3-5 times. The dialysis bag was stored immersed in a 50% ethanol solution at 4 °C.

2.2. Materials Characterization
The main instruments used were a Tecnai G2 F20 S-TWIN transmission electron microscope (FEI, USA), a 1-24LSC freeze dryer (Martin ChristDelta, Germany), a RF-5301PC fluorescence spectrophotometer (Shimadzu (Hong Kong) Company.), a Fourier infrared spectrometer (Perkin Elmer Singapore), a UV-2550 UV-Vis Spectrophotometer (Shimadzu (Hong Kong) Company), a H1650-W high speed desktop centrifuge (Hunan Xiangyi Laboratory Instrument Development Company), a HYJX-100ml homogeneous reactor (Weihai Huanyu Chemical Machinery Company) and a dialysis bag (relative molecular mass of 1000 Da).

3. Results and Discussion
Figure 1 shows that the carbon quantum dots are uniformly distributed in the solution. The carbon quantum dots are approximately spherical with a diameter of about 3 nm, and they are relatively uniformly dispersed. The fluorescent carbon quantum dot particles synthesized from glucose using this one-step hydrothermal method have small sizes and a uniform distribution, so high-quality carbon quantum dots can be obtained relatively easily. Figure 2 shows the infrared spectrum of the CQDs. It can be seen from figure 2 that there are significant absorption peaks at 3278 cm\(^{-1}\), 2898 cm\(^{-1}\), 1453 cm\(^{-1}\), and 1014 cm\(^{-1}\). The absorption peak at 3278 cm\(^{-1}\) can be assigned to an O-H stretching vibration, possibly from a hydroxyl group, At 2898 cm\(^{-1}\) can be assigned to an C-H stretching vibration, The absorption peak at 1453 cm\(^{-1}\) is a C=O Characteristic peak and the absorption peak at 1014 cm\(^{-1}\) is a C-O Characteristic peak. These results indicate that the surface of CQDs contains hydroxyl and carboxyl functional groups.
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Figure 1. TEM image of the CQDs.

Figure 2. Infrared spectrum of the CQDs.

The Ultraviolet spectra of the CQDs prepared at multiple reaction temperatures are shown in figure 3. The CQDs show significant optical absorption in the ultraviolet region that extends into the visible region. Most carbon quantum dots have broad absorption in the 260-320 nm range [14]. According to figure 3 that the maximums of the UV absorption peaks of the CQDs appear at 294 nm, 298 nm, 301 nm, and 287 nm when the reaction temperatures are ranges from 160 °C to 220 °C, with an interval of 20 °C. At 160 °C to 200 °C, the peak position is red-shifted; between 200 °C and 220 °C, the peak position is blue-shifted. Comparing the four reaction temperatures, the peak position is red-shifted the most when the CQDs were prepared at 200 °C.

The Ultraviolet absorption spectra of the CQDs prepared at multiple reaction times are shown in figure 4. According to figure 4 that the maximums of the UV absorption peaks of the CQDs appear at 285 nm, 287 nm, 301 nm, and 288 nm when the reaction times from 4 h to 10 h, and 2 h was an interval. Reaction times range from 4 to 8 hours, the peak position is red-shifted; Reaction times range from 8 to 10 hours, the peak position is blue-shifted. Comparing the four reaction times, the peak position is red-shifted the most for a reaction time of 8 h.

Figure 3. UV-vis spectrum of the CQDs prepared at multiple reaction temperatures.

Figure 4. UV-Vis spectra of the CQDs prepared at multiple reaction times.

Figure 5 shows the fluorescence intensity of the CQDs prepared from 4 h to 10 h, and 2 h was an interval. Figure 6 shows the effect of reaction time on fluorescence intensity. As can be seen from the
Figure 6, when the reaction time reached 8h, the fluorescence intensity showed an increasing trend, which yields the strongest fluorescence intensity, and then begins to decrease with longer reaction times. Thus, the fluorescence intensity was strongest with a reaction time of 8 h.

Figure 5. Fluorescence spectra of the CQDs prepared with multiple reaction times.

Figure 6. Effect of the reaction time on the fluorescence intensity of the CQDs.

Figure 7 shows the fluorescence intensity of the CQDs prepared from 160 °C to 220 °C, with an interval of 20 °C. Figure 8 shows the effect of reaction temperature on fluorescence intensity. From the figure, the fluorescence intensity initially decreases and then increases with increasing temperature. When the reaction temperature is 200 °C, obtain the strongest intensity. Thus, the optimal temperature for the reaction is 200 °C.

Figure 7. Fluorescence spectra of the CQDs prepared at multiple reaction temperatures.

Figure 8. Effect of the reaction temperature on the fluorescence intensity of the CQDs.

Figure 9 shows the normalized fluorescence spectra of the CQDs measured at multiple excitation wavelengths, using excitation wavelengths at intervals of 20 nm between 300 nm and 420 nm. It can be seen from the figure that the emission peak wavelength shifts slightly when the excitation shifts from 300 nm to 320 nm, and the red shift occurs when the wavelength increases from 320 nm to 420 nm, indicating that the prepared CQDs have some excitation wavelength dependence.
4. Conclusions
In this paper, Carbon quantum dots was prepared by one-step hydrothermal method with glucose as carbon source. The effects of the reaction temperature and reaction time on the CQDs were investigated. The optimal parameters for the CQD synthesis were determined using UV absorption spectroscopy and fluorescence spectrum. The fluorescence intensity of the CQDs was maximized at 200 °C and 8 h. A uniform particle size distribution of about 3 nm was obtained. The infrared spectrum analysis shows that CQDs contains a variety of oxygen-containing groups, including hydroxyl groups and carboxyl groups. These functional groups can be functionalized using various organic, inorganic or biological materials through covalent bonds, hydrogen bonds and electrostatic interactions. This provides the opportunity to further expand the applications of CQDs in the fields of analysis and testing.

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