Controllable synthesis of Graphene Quantum Dots with Tunable-Photoluminescence

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Abstract. Graphene quantum dots (GQDs) have been synthesized via one-pot hydrothermal approach using glucose as precursors. The obtained products have a size around 3.5 nm, which can be controlled by changing the reaction temperature. With the increase of preparation temperatures, the glucose molecules are dehydrated under hydrothermal conditions and then converted to GQDs. The high temperature helps to increase the graphitization degree of GQDs. The GQDs show the blue color emission under excitation of 300-450 nm, which can be used in electrochemical luminescence devices.

1. Introduction
Graphene quantum dots (GQDs) have aroused wide attention because of its unique optical properties, including tunable photoluminescence and high biocompatibility [1-6]. It provides unprecedented opportunities for bioimaging and optical sensing [7-11].

As for the GQDs, many preparing methods, including “top–down” and “bottom–up” [12-17]. However, most “top–down” methods, including cutting graphite crystallites using electrochemistry methods usually suffer from some disadvantages. Herein, we report the GQDs prepared via a simple one-pot “bottom–up” hydrothermal approach using glucose as precursors. With the control of other variables, the final size distribution of products can be effectively controlled by tuning the reaction temperature. Besides, these GQDs have nearly excitation-dependent blue intrinsic emissions.

2. Experiments and results
In the procedure of GQDs preparation, 0.5 g glucose and 10 ml H2SO4 were added into 10 ml deionized water. The mixture was treated in reaction kettle at 220 ℃ for 3 h. Then, the sample was neutralized with sodium hydroxide and purified by a dialysis tube (1000 Da).

Transmission electron microscopy (TEM, JEM2100F) and atomic force microscope (AFM, NT-MDT Prima) were measured to characterize structure of GQDs. Fourier transform infrared spectra (FTIR) were measured to find the chemical bonds of GQDs. Raman scattering spectra were performed on a Jobin Yvon Lab RAM HR spectrometer using 325 nm line of Ar ion laser. Photoluminescence (PL) spectra were performed by Hitachi F-7000. UV-visible spectra were performed by a Perkin-Elmer Lambda 20 spectrometer.

Figure 1 (a) and (b) show the representative TEM images and Statistical analysis of the GQDs. It can be observed that the as prepared GQDs exhibit an average size of around 3.5 ± 1.0 nm. This can be regarded as direct evidence for the formation of GQDs.
Figure 1 (a) TEM image of the GQDs and size distribution of GQDs (b).

Figure 2 (a)-(d) show the TEM images obtained at different preparation temperatures. It can be clearly observed that GQDs are spherical and uniformly dispersed in aqueous solution. Meanwhile, with the increase of preparation temperatures from 160 to 220°C, the size and the number of GQDs increases significantly. The variation of GQDs size and number can be attributed to the high temperature, which provides more reaction power. Therefore, the glucose molecules are dehydrated under hydrothermal conditions and then converted to GQDs. Moreover, more and more small GQDs agglomerates to form larger GQDs.

Figure 2 TEM image of the GQDs (red circles) obtained at different preparation temperatures, 160°C (a), 180°C (b), 200°C (c), 160°C(d).

FTIR is used to characterize the obtained GQDs at different preparation temperatures. All the GQDs show the absorption of O-H, C=C, C-H and C-O groups, suggesting that the GQDs contain some incompletely carbonized glucose. Additionally, it should be noted that, with the increase of GQDs preparation temperatures from 160 to 220°C, the absorption intensity of the O-H groups is weakened. Moreover, the absorption intensity of the C=C groups are greatly enhanced. All these results demonstrate that the number of GQDs increases significantly in high temperatures. Figure 3 (b) shows the Raman spectra of the GQDs at different preparation temperatures. The D band corresponds to the disordered carbon and the G bands associated with the graphitic layers. Low intensity ratio of \( \frac{I_D}{I_G} \) indicates a high degree of graphitization [18-20]. With the increase of temperature, the \( \frac{I_D}{I_G} \) ratio decreases from 0.31 (200°C) to 0.20 (220°C). This phenomenon can be attributed to that high temperature promotes the formation of high graphitization degree. Compared with the Raman spectra of 200 and 220°C, the Raman of 160 and 180°C have no obvious D band, it can be attributed to the less amount of GQDs.

Figure 3 FTIR (a) and Raman spectra (b) for GQDs obtained at different preparation temperatures.
Figure 4 (a) presents the PL spectra (E_X = 420 nm) of GQDs obtained at different preparation temperatures. It can be clearly observed that GQDs (220°C) exhibit a maximum PL intensity. Meanwhile, with the increase of preparation temperatures from 160 to 220°C, the PL intensity increases significantly and the maximum PL position of the GQDs exhibit barely shifted, which can be attributed to the increase of GQDs amount. Besides, the oxygen-containing groups play a role as the PL intensity of GQDs. With the increase of preparation temperatures, the glucose molecules are further dehydrated under hydrothermal conditions and then converted to GQDs. The new formed GQDs may have similar size distribution and surface states to those GQDs. Therefore, the increase of preparation temperatures can increase the PL intensity of GQDs, but has nearly no effect on the PL wavelength. These results further confirm that high quality GQDs can be prepared by adjusting the temperature.

Figure 4 (b) shows a detailed PL investigation with different excitation wavelengths. When the excitation wavelength is changed from 300 to 450 nm, the PL spectra of GQDs exhibit shifts in emission peaks, demonstrating that all PL emission peaks were dependent on the excitation. The excitation-dependent PL behavior is considered be related to surface defects of GQDs. UV-Vis absorption and PLE spectroscopy revealed the characteristic bands associated with as-prepared GQDs. As shown in Figure 4 (c), the UV-visible absorption of GQDs shows a strong absorbance in the range of deep UV that locates at 220 nm which is assigned to the π-π* transition of C=C bonds. The PLE spectrum detected at 520 nm shows a distinct peak at 420 nm, corresponding to the absorption peaks at 220 nm. Moreover, the GQDs dispersion appears blue color under illumination of UV (365 nm).

3. Conclusions
In summary, graphene quantum dots synthesized by a controllable hydrothermal approach using glucose as precursors. The size distribution and graphitization degree of GQDs have been studied in detail, it can be controlled by changing the preparation temperatures. The GQDs show the blue color emission under excitation of 300-450 nm, which can be used in electrochemical luminescence devices.

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