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Thermal reduction effects on one- and two-photon luminescence in graphene quantum dots

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ABSTRACT

Thermal reduced graphene quantum dots (GQDs) have been synthesized and investigated based on various heating temperatures. The characterizations of GQDs' size, crystallization and oxygen group confirm the thermal reduction influences. In experiment, GQD solutions display broad UV–vis absorption and good one-photon luminescence phenomena. Moreover, thermal treatment with higher temperature makes a blue-shift phenomenon in optical properties. Additionally, good two-photon luminescence properties can be observed with the treatment of lower thermal temperatures. First-principle calculations theoretically confirm that the sizes and oxygen groups can affect the band gaps and orbital's distributions. The observed good one- and two-photon luminescence properties can be potential for future bioimaging applications.

1. Introduction

Graphene quantum dots (GQDs) is a remarkable material due to its feasible solution-preparation, ultrathin structure, and tunable band gap [1–3]. GQDs exhibit good absorption and luminescence for potential optical applications [4–11]. GQDs' non-toxicity and biocompatibility make them a candidate for future biological and biomedical fields [12–16].

Furthermore, carbon-based nanomaterials, including nitrogen-doped GQDs [17], surface-passivated carbon dots [18] and poly-ethylene-glycol-linked graphene oxide nanoparticles [19], can possess two-photon luminescence, which has begun to attract intensive interests, because of the great potential applications in the bioimaging of a penetration depth of living organism [20,21].

Top-down and bottom-up approaches, such as strong acid [6], hydrothermal [22], and reaction of organic compounds [2], have been developed for the syntheses of different sizes and shapes of GQDs and also tune the electronic and optical properties. Hummers method [23] is widely used for the fabrications of graphene oxide (GO). Chemical or thermal reduction is always used to prepare reduced GO, since such approach is simple to modify the size, shape and fraction of sp^2 domains [24]. In this work, we experimentally synthesize GQDs following the modified Hummers method and then investigate thermal reduction effects on the optical properties of GQDs including their one- and two-photon luminescence.

2. Results and discussion

GQDs were prepared from CX-72 carbon black by the modified Hummers method [23] (Supplementary material, S1). To investigate the thermal reduction effect, the samples were reduced at different temperatures including 200 °C, 300 °C, 350 °C, 400 °C, and 500 °C for 30 min, and then cooled down to the room temperature.

The sizes of GQDs are grown with the enhanced temperatures, characterized by transmission electron microscopy (TEM) (Fig. 1(a)–(e)). At 200 °C, 300 °C and 350 °C, the corresponding GQD sizes are around 3–5 nm, 20–40 nm and 50–75 nm. When the temperature is 400 or 500 °C, the sizes are larger than 100 nm. It is also noticed that with the increase of the temperature, the uniformity of the sizes becomes bad. With the treated temperature of 200 °C, the sharp (002) lattice peak centered at 22.4° was characterized by X-Ray powder diffraction (XRD) (Fig. 1(f)), exhibiting that the GQDs have formed a uniform crystalline structure. After heightening the temperature to 300 °C or 350 °C, a broad (002)

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peak at 24.3°, corresponding to the graphite generating, can be seen. The higher the treated temperature is, the smaller the peak is. When the temperature reaches 500 °C, the (002) peak could barely be seen. The XRD results reveal that the process of thermal reduction treatment has affected the lattice structure and also display a trend that the crystallization of GQDs becomes worse with the rising temperature.

Functional groups of GQDs were characterized by Fourier transform infrared spectroscopy (FTIR), as shown in Fig. 2(a). No obvious changes can be found with the temperature rising from 200 °C to 300 °C. When the temperature approaches to 350 °C, a small free hydroxyl characteristic peak appears at 3730 cm^{-1}, revealing that a small amount of free hydroxyl groups begins to generate during the thermal treatment. The carbonyl characteristic peak at 1722 cm^{-1} reaches maximum. With the temperature rising up to 400 °C, the free hydroxyl characteristic peak of 3730 cm^{-1} still exists. By contrast, the carbonyl characteristic peak at 1722 cm^{-1} and the C–O peak at 1252 cm^{-1} disappear. The FTIR line of 500 °C is similar to that of 400 °C. Herein, the peaks centered at 1722 cm^{-1} and 1252 cm^{-1} existing from 200 °C to 350 °C indicate that with the increase of temperature carbon–oxygen groups vanished gradually.

Moreover, with the characterization of X-ray photoelectron spectroscopy (XPS) (Fig. 2(c) and Table S1), it is clearly shown that with the increase of the treated temperature, the ratio of oxygen decreases while the ratio of carbon increases. As shown in the C1s spectra of GQDs (Fig. 2(d)), the sp^2 carbon–carbon networks, characterized as 284.5 eV are enhanced, while carbon–oxygen groups, characterized as 286.5 eV for C–O and 287.5 eV for COOH, are decreased. Meanwhile, the ratio of C–O becomes more dominated in comparison to that of COOH.

Fig. 2(b) shows ultraviolet visible (UV–vis) spectra of GQD solutions at different temperatures, exhibiting a broad UV–vis absorption from 200 nm to 700 nm. The curve of GQDs at 200 °C possesses three shoulders at 226 nm, 300 nm and 420 nm respectively. When the temperatures are 300 °C and 350 °C, the curves display blue-shift phenomenon. When the temperature becomes 400 °C or 500 °C, the corresponding UV–vis absorption decreases severely. Herein, with the increase of temperature, the blue-shift phenomenon becomes more obvious. By contrast, the intensity of UV–vis absorption of GQDs solution is poorer.

The photoluminescence (PL) curves of GQD solution based on one-photon absorption at different temperatures are shown in Fig. 3. The emission peaks locate around 520 nm with the excitation wavelength of 250 nm, 280 nm, 300 nm, 365 nm, 400 nm, and 470 nm when the temperature is 200 °C. Additionally, the strongest intensity occurs with the excitation of 470 nm. When the temperature is 300 °C, PL intensity decreases apparently. When the temperature reaches 350 °C, PL intensity decreases further and the strongest emission intensity is observed with the excitation of 250 nm. When the temperature is larger than 350 °C, PL is hard to be observed with the excitation wavelength larger than 365 nm.

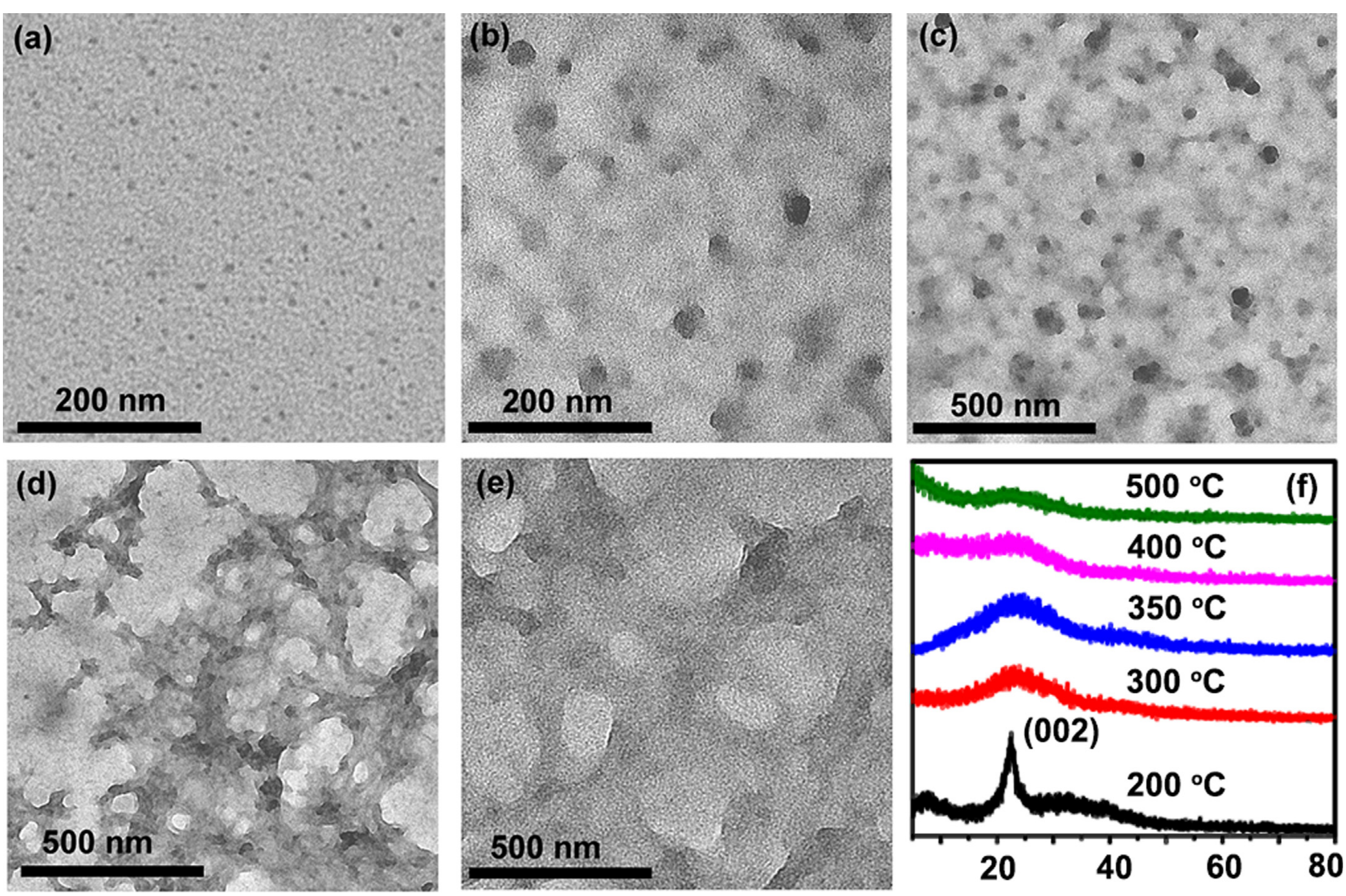

Fig. 1. (a)–(e) TEM images at 200 °C, 300 °C, 350 °C, 400 °C and 500 °C. (f) XRD of GQD at different temperatures.