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Size controllable preparation of graphitic quantum dots and their photoluminescence behavior

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ABSTRACT

To control the size of graphitic quantum dots (GQDs), an electrochemical method was successfully developed with applied potentials cycling between -5.0 and 5.0 V at various scan rates from 0.2 to 0.5 V/s. The average size of the resultant GQDs decreases from 12 to 3.4 nm with increasing scan rates, as verified by their transmission electron microstructure (TEM) images. The X-ray diffraction (XRD), optical absorption, photoluminescence (PL), Fourier Transform Infrared (FTIR) and photoluminescence excitation (PLE) behaviors of those GQDs were investigated. The result shows that the $n-\pi^*$ electronic transition resulting from the surface oxygen groups contributes to the PL emission, besides the $\pi-\pi^*$ electronic transition due to their sizes.

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1. Introduction

The fluorescent carbon family, such as shortened carbon nanotubes, amorphous and crystalline carbon dots, and graphene quantum dots (GQDs) shows photoluminescence (PL) characteristics [1], opening their applications in optical/photovoltaic devices, energy efficient displays and lightning [2], and bioimaging [3]. GQDs have been considered as one of the most promising nano-materials due to their environmental-friendliness [4], high water solubility [5], high photostability, and resistance to metabolic degradation in bioapplications and excellent electrical/optical properties [6]. Numerous methods have been reported for GQDs preparation, such as nanolithography [7], hydrothermal process [8], chemical exfoliation [9], electrochemical oxidation method [10,16], and UV irradiation and sonication assisted hummer method [11]. Nevertheless, due to the uncertainty on formation mechanisms precise control over the sizes of GQDs still remains a challenge [12]. Herein, we propose a new strategy to achieve size-controllable GQDs by adjusting the scan rates within certain range of applied potentials in the electrochemical process.

On the other hand, most of the experimental work has been focused on the preparation and the improvement of quantum yields [13]. The mechanism of PL is still under intensive discussion, varying from case to case [14]. For instance, the explanations of

λ_{ex} -dependent or independent PL of GQDs and their origin were widely discussed and generally classified into two catalogs including core related and surface state related emission [15]. In this work, the effects of size and surface oxygen groups on the PL of GQDs were studied and a surface oxygen group related luminescence mechanism was proposed.

2. Results and discussion

As-prepared GQDs show almost the same spherical shape for various scan rates from 0.2 (GQD_{0.2}) to 0.3 (GQD_{0.3}), 0.4 (GQD_{0.4}) to 0.5 (GQD_{0.4}) V/s, but they differ in their sizes (Fig. 1). Experimental details can be found in the online supplementary materials. GQD_{0.2} shows an average size of 12 nm, but with increasing scan rates, their average sizes decrease to 9 , 5.3 and 3.4 nm for GQD_{0.3}, GQD_{0.4} and GQD_{0.5}, respectively. Particularly GQD_{0.2} demonstrates that $>40\%$ of them predominantly distributed at a diameter of 12 nm, which is apparently larger than the other GQDs.

X-ray diffraction (XRD) (Fig. 2) shows the characteristic (002) diffraction of the GQDs at 2θ of ca. 23.5° , agreeing well with previous work [10]. Slight increases of full width at half maximum (FWHM) of GQDs with scan rates from 0.2 to 0.5 V/s confirm the reduction of GQDs sizes. Detailed mechanism of controlling the sizes of GQDs is in the electronic supplementary material.

Size differences are further verified by their UV-vis absorption spectra (Fig. 3f), i.e. the GQD_{0.2} shows red-shift to ca. 221 nm

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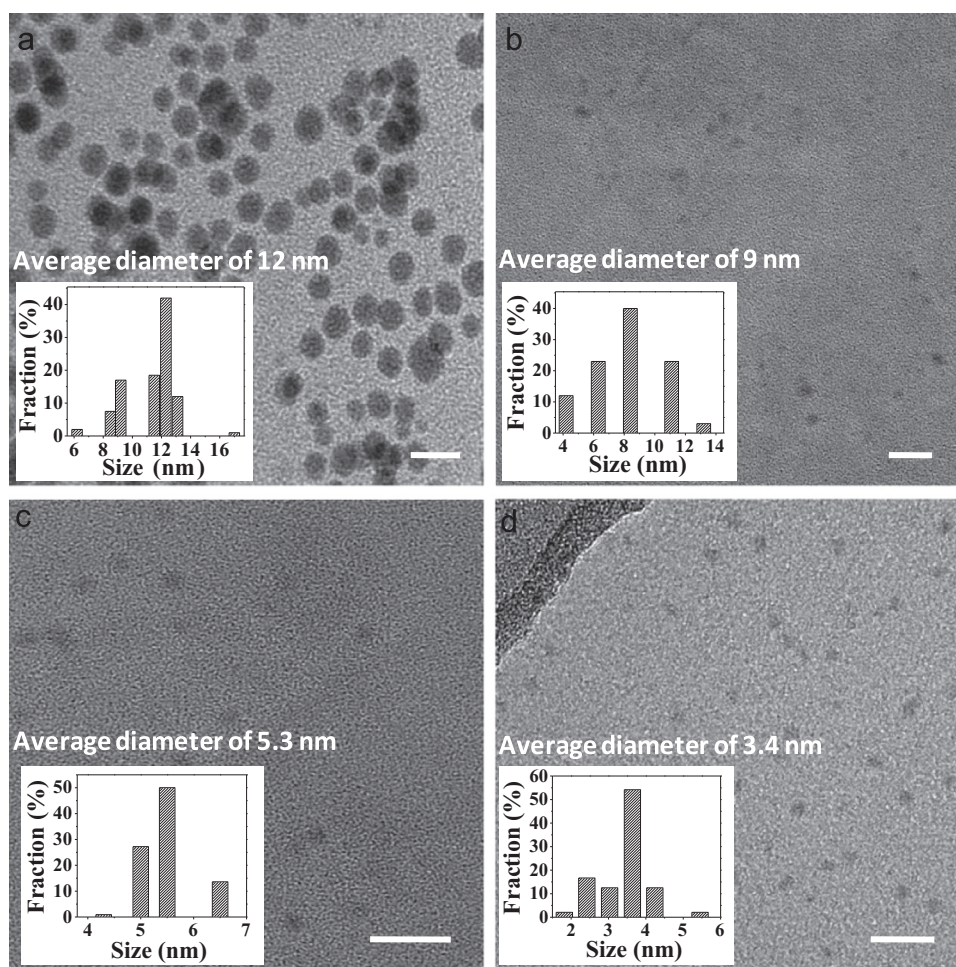


Fig. 1. TEM images of GQDs prepared using applied potentials cycling between -5.0 and 5.0 V at various scan rates from 0.2 to 0.5 V/s: (a) $\text{GQD}_{0.2}$, (b) $\text{GQD}_{0.3}$, (c) $\text{GQD}_{0.4}$ and (d) $\text{GQD}_{0.5}$. Scale bars = 20 nm, insets are size distribution of each corresponding GQDs with calculated average sizes.

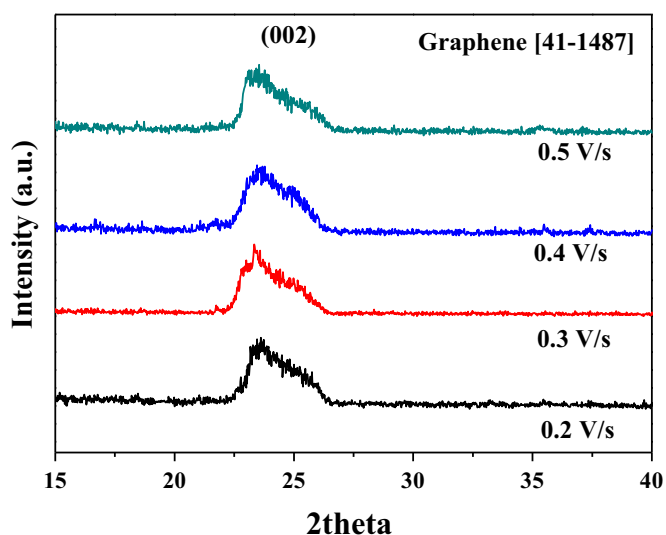


Fig. 2. XRD of GQDs prepared at different scan rates ranging from 0.2 to 0.5 V/s.

whereas the absorption peaks of the other three GQDs-solutions located at ca. 206 nm identically. Generally, the peak below 270 nm is corresponding to the π - π^* transition of the aromatic sp^2 domains. Therefore, the aromatic sp^2 domains of $\text{GQD}_{0.2}$ are larger than that of the other three GQDs, agreeing well with its TEM (Fig. 1a). In contrast, the other three smaller GQDs have different

sizes (Fig. 1b–d), but they show identical absorption peaks, indicating the π - π^* transition behaviors are similar when the sizes reduced to certain range, i.e. 3.4 – 9 nm in this case.

Usually, the UV-vis and PL spectra exhibit red shift as increasing the particle size of nanomaterials. Although the red-shift of UV-vis spectra was observed when the average size ≥ 12 nm, all the GQDs emitted the same blue-green luminescence on being excited by a 365 nm lamp (Fig. S1). This mismatch between sizes and luminescence was further investigated by PL spectra on the GQDs-solutions. These GQDs showed almost the same excitation-dependent PL emissions (Fig. 3a–d), as reported previously [17]. Further observation showed that the emission peak positions almost unchanged at 445 nm on being excited by the same wavelength at 360 nm (Fig. 3e), reflecting their PL may originate from their similar surface oxygen groups [18]. This phenomenon at least confirms that the sizes of GQDs had little influence on the PL emission when reducing to such ranges as 3.4 – 12 nm.

To explain the mismatch between same PL emission and different sizes of the prepared GQDs, the PLE spectra of the GQD solutions were examined. According to the emission peaks in the PL spectra, the wavelengths of 440 nm were selected as the detection wavelength. As shown in Fig. 3e, $\text{GQD}_{0.2}$ displayed one single broad shoulder peak at 340 nm, which might be the combination of the red-shifted π - π^* and the locally existed n - π^* electronic transitions [22]. $\text{GQD}_{0.3}$ and $\text{GQD}_{0.4}$ demonstrated their broad peaks at ca. 270 nm and the other shoulder peaks at ca. 340 nm. The broad peak of $\text{GQD}_{0.5}$ slightly blue-shifted to 263 nm, but its shoulder peak remained at ca. 340 nm. Same locations of

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