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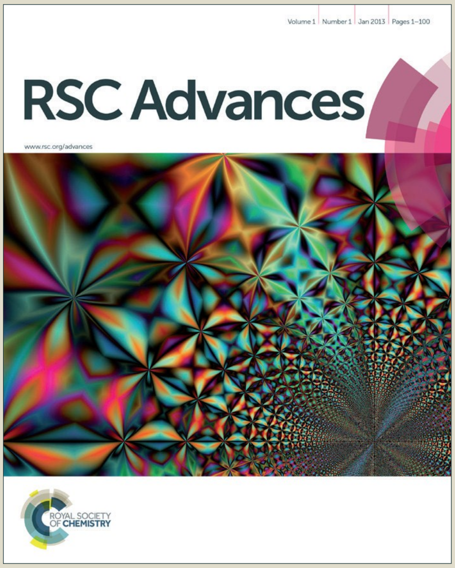

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Large Scale Preparation of Graphene Quantum Dots from Graphite Oxide in Pure Water *via* a One-step Electrochemical Tailoring

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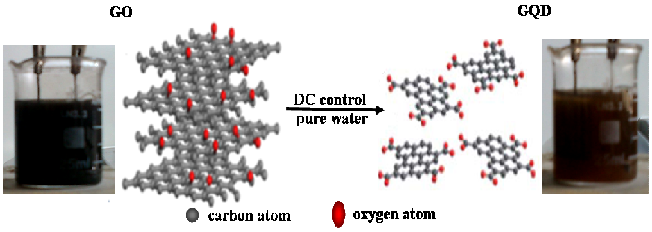
A novel electrochemical synthesis for graphene quantum dots (GQD) with large scale from graphite oxide (GO) in pure water has been proposed. GQDs with different sizes and different emission colors were obtained with a yield of 65.5% in weight, which exhibited intrinsic peroxidase-like activity in glucose detection.

Graphene quantum dots (GQD), a new kind of fluorescent carbon nanomaterials consisting of a graphite-structure, has attracted tremendous interest because of its unique properties, such as high surface area, low toxicity and superior optical properties etc.[1-4] Due to its significant properties, GQD has been proved to be potential candidates for bioimaging, chemical and biological sensing,[5, 6] photocatalyst,[3, 7] electrocatalyst and so on.[8, 9] Generally, there are two ways for preparation of GQD. One is the bottom-up route: Li's group has made great effort to prepare GQD by stepwise solution chemistry based on oxidative condensation reactions;[10, 11] and organic precursors were applied to synthesize GQD by carbonization.[12] The other is top-down route: acidic oxidation of carbon-containing material was adopted by several groups to prepare GQD,[13, 14] hydrothermal and solvothermal treatments were also used to synthesize GQD.[15, 16] Compared with these methods, electrochemical method is advantageous for its low cost, ecology and easy manipulation. Li *et al.* used filtration-formed graphene film as the working electrode upon the application of cyclic voltammetry (CV) scan in phosphate buffer solution to prepare GQD with a uniform diameter of 3-5 nm.[17] Bao and co-workers prepared GQD by electrochemical etching carbon fibers at a constant potential for several hours in acetonitrile solution.[18] Shinde and co-workers reported one two-step process for the electrochemical transformation of multi-walled carbon nanotubes to GQD.[19] However, the above electrochemical methods need a electrode with graphene-like materials, and could not synthesize GQD with large scale.

Recently, our group has proposed a facile electrochemical carbonization of small molecular, but it was not environment-friendly because a large mount of chemical reagents were used as the electrolyte.[20] Efficient and environment-friendly synthesis is important for its further study and application. Herein, a large scale, economical and efficient electrochemical synthesis of GQD from graphite oxide (GO) was reported. The pure water was saved as the electrolyte without any assistance of other chemical reagents. The yield of GQD was about 65.5% in weight with different sizes and emission colors, for example purple-blue ($GQD_{purple-blue}$), blue (GQD_{blue}) and green (GQD_{green}) GQDs were obtained from the raw production through dialysis. Moreover, resultant GQD possesses excellent peroxidase-like activity for the reduction of hydrogen peroxide.



Scheme 1 Illustration of the preparation of GQD from graphite oxide.

Scheme 1 displays the preparation scheme of GQD from GO. Unlike traditional electrochemical method using graphite-based materials as the electrodes, two Pt sheets were used as the anode and cathode here. GO powder as reactant and pure water saved as electrolyte without any other chemical reagent. In our strategy, the whole synthesis involved a disorder electrochemical etching process. The constant voltage mode was used (15 V). As the GO changed into GQD, the conductivity of the electrolyte changed and the current intensity varied in range of 30-50 mA/cm^2. Under stirring, the black GO solution turned into brown raw GQD solution after electrochemical reaction for about 3 h (picture in Scheme 1). Our design improved the productivity of GQD greatly with the yield of 65.5% in weight. As previous study,[21-23] hydroxyl and oxygen radicals originated from anode are the key for the cleavage of graphitic structure into small GQD. In present process, the voltage applied in the experiments was high enough to oxidize the water to generate hydroxyl and oxygen radicals. Abundant of hydroxyl and oxygen radicals arose at anode, which could absorb on GO and ruin the structure of GO under stirring, GQD was obtained finally.[21-23]

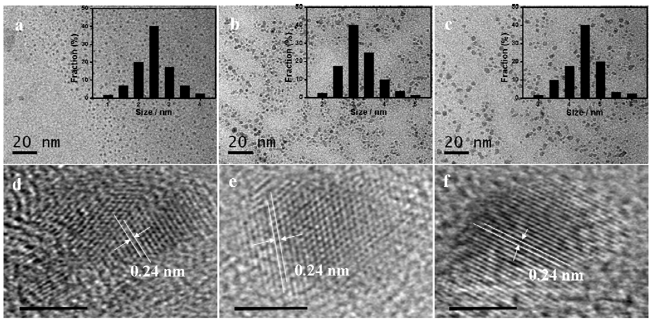


Figure 1 TEM images of $GQD_{purple-blue}$ (a), GQD_{blue} (b) and GQD_{green} (c), respectively. The inserts are corresponding size distribution. HRTEM images of $GQD_{purple-blue}$ (d), GQD_{blue} (e) and GQD_{green} (f), respectively. The scale bar of (d-f) is 2 nm.

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Through simple dialysis, GQD with different sizes and emission colors were obtained (the fraction of 1000-3500 Da for $GQD_{purple\text{-}blue}$, fraction of 3500-7000 Da for GQD_{blue} and fraction >7000 Da for GQD_{green}). Figure 1(a-c) shows typical transmission electron microscopy (TEM) images of GQDs with different sizes. These images reveal that the as-synthesized GQD are uniform and monodisperse. The size distribution exhibits that their average diameters centered at about 2.4 ± 0.3, 3.6 ± 0.2 and 4.6 ± 0.4 nm, respectively. The high resolution TEM (HRTEM) image (Figure 1(d-f)) displays the clear lattice structure of GQD, indicating their high crystallinity. Their lattice parameters were measured to be about 0.24 nm, corresponding to the [1120] lattice fringes of graphite.[13] The [002] crystal phase of graphite has not been observed, indicating that as-prepared GQDs have only one or few layers of graphene sheet.[24] Figure S1 shows the typical X-ray diffraction (XRD) patterns of different GQDs. The GQDs have a broad peak centered at around 23°, which was attribute to disorder graphitic structure resulting from electrochemical oxidation process of GO.[25] These results demonstrate that GO could be etched into GQD, suggesting our strategy is an efficient and powerful method to prepare GQD.

The chemical composition and structure of GQD and GO were further characterized by Fourier-transform Infrared (FT-IR) and Raman spectra. The FT-IR spectra of GQD and GO did not show any obvious difference (see Figure S2, Supporting Information, SI): peaks at 3430 and 1690 cm^{-1} are associated with the vibrations of O-H and C=O bonds,[20] respectively, while the absorption peaks at 2955 and 1210 cm^{-1} are corresponding to C-H and C-O bond.[12] This result reflects that GQD have many oxygenated functional groups such as carboxylic acid, alkoxy, hydroxyl and carbonyl groups on their surfaces. Raman spectrum of GQD has a D-band at 1360 cm^{-1} and a G-band at 1630 cm^{-1} with an intensity ratio I_D/I_G of 1.19 (see Figure S3, SI), which is much higher than that of GO (I_D/I_G of 0.85). This result implies that numerous structural defects capped with various oxygenated groups exist on the surfaces of GQD.[13, 18, 26] XPS spectra result (Figure S4) was in agreement with that of Raman spectra: the ratio of oxygen in GQD was higher than that of GO obviously, which should be induced by electrochemical oxidation and etching of the GO.[18, 20, 27]

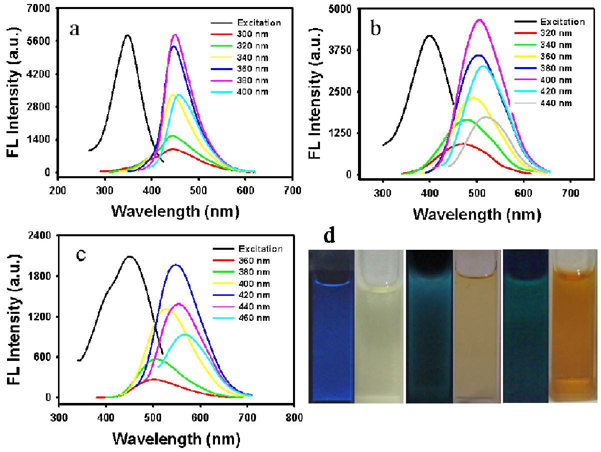

Figure 2 FL spectra of $GQD_{purple\text{-}blue}$ (a), GQD_{blue} (b) and GQD_{green} (c), respectively. (d) The digital pictures of $GQD_{purple\text{-}blue}$, GQD_{blue} and GQD_{green} (from left to right), respectively. The concentration of GQD in water were 0.05 mg/mL, the pH was 7.0 and the slit width 5 nm.

The optical properties of GQD were investigated by ultraviolet visible (UV-vis) absorption spectroscopy (Figure S5, SI) and fluorescence (FL) spectroscopy (Figure 2). A well-defined UV-vis absorption near 300 nm could be ascribed to the π-π transition of aromatic sp^2 domain within the GQD.[20] As shown in Figure 2a-c, the GQD exhibits a typical excitation-dependent FL behavior, which was very similar to previously reported GQD. For $GQD_{purple\text{-}blue}$, the emission peak shift from 444 nm to 457 nm when excitation varied from 300 nm to 400 nm. The emission peak of GQD_{blue} shift from 470 nm to 520 nm when excitation varied from 320 nm to 440 nm. And the emission peak of GQD_{green} shift from 500 nm to 560 nm when excitation varied from 360 nm to 460 nm. Figure 2d shows the digital photographs of $GQD_{purple\text{-}blue}$, GQD_{blue} and GQD_{green} under 365 nm excitation and sunlight. The purple-blue, blue and green emission colors for three GQDs were observed. The brightness of GQDs is different, indicating that the GQDs have different quantum yields (as summarized as Table S1, SI). The quantum yield of $GQD_{purple\text{-}blue}$ at 380 nm excitation was calculated to be about 7.8% by calibrating against quinine sulfate. According to the previous studies,[20, 28] the shift in emission peak positions with different excitation wavelengths arose from different emissive sites on GQDs. At certain excitation wavelengths, some corresponding emissive sites would be excited and fluoresce, resulting in the excitation-dependent behaviors of emission spectra.[18] The fluorescence spectra of GQD could reflect the distribution of emissive sites on the GQD, and also the size effect. The photoluminescence mechanism of GQD could be quantum-confinement effects, emissive traps, electronic conjugate structures, and free zig-zag sites.[22, 29] However, the certain photoluminescence mechanism of GQD is still under investigation.

To further explore the optical properties of GQDs, a detailed FL study was obtained in water of different pH and temperature (Figure S6a-b, SI). The fluorescence intensities of GQDs were pH independent under acidic conditions, while decreased in basic condition. Also the fluorescence intensities of GQDs were temperature independent when the temperature was blow 60 °C. Otherwise, the fluorescence intensities of GQDs were stable for more than a month without any distinct reduction (Figure S6c, SI). As mentioned above, abundant oxygen-containing functional groups exit on the surface of GQDs, which improve the hydrophilicity and stability of them in aqueous solution. Additionally, GQDs show excellent photostability, and the fluorescence intensity did not change even after continuous excitation with a 150 W Xe lamp (Figure S6d, SI). These optical properties indicate the tremendous practical application potential of GQDs.

The peroxidase-like activity of GQD was evaluated in the catalysis for oxidation of peroxidase substrates TMB in presence of H_2O_2. As shown in Figure 3, the absorption intensity (652 nm) of TMB-GQD-H_2O_2 system was much higher than that of the TMB-H_2O_2 and TMB-GQD systems. Additionally, the absorbance at 652 nm increased with increasing H_2O_2 concentration (Figure S7a-b, SI). Besides TMB, GQD could catalyze the oxidation of other peroxidase substrates *o*-phenylenediamine (OPD) and pyrogallol and produce the typical color reaction (Figure S8, SI). Up to now, there are few reports about GQD as enzymatic mimetics. Researchers believed that the catalytic mechanism was probably originated from an increase in the electron density and mobility in the GQD from lone-pair electrons in amino groups of peroxidase substrates to GQD.[30] Based on these results, GQD was used for glucose detection successfully (Figure S7c-d, SI). When glucose was in range of 0.25-50 μM, there was a good linear

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relationship between increased absorbance at 652 nm and the concentration of glucose (R^2=0.9923). The detection limit is as low as 0.1 μM (S/N=3). All these results suggest that as-prepared GQD possess excellent peroxidase-like activity, indicating the tremendous biochemical application potential.

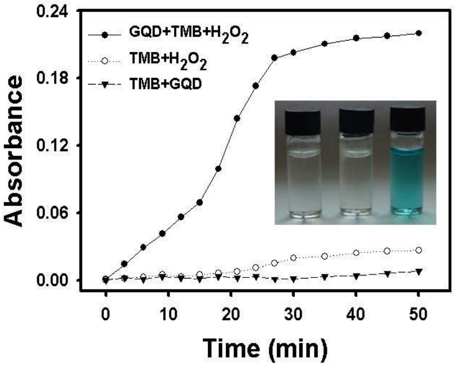

Figure 3 Time-dependent absorbance changes of TMB at 652 nm in different assays. Inserts are the digital pictures of them: (from left to right) TMB-GQD, TMB-H_2O_2 and TMB-GQD-H_2O_2, respectively. The pH of NaAc buffer was 4.0; the concentration of GQD was 1 μg/mL. The concentration of TMB was 0.8 mM, and H_2O_2 was 0.05 mM. Before absorbance test, all the samples were kept in 35 ^{o}C water bath for 30 min.

In summary, we demonstrate a facile and economical modified electrochemical method for preparation of GQD from GO with large scale. The yield of GQD was as high as 65.5%. Hence, this method is simple, easily controllable and readily scalable to industrial levels. GQD with different sizes and emission colors exhibited excellent peroxidase-like activity, suggesting the potential of application in biosensors.

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