Supporting Information

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

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Apparatus and reagents

A PS-305DM constant-current supply (LongWei Instrument Co., LTD, HK) was used for synthesis of GQD. F-4500 Fluorescence spectrophotometer (Hitachi Co. Japan) was used to collect the fluorescence spectra. The ultraviolet-visible (UV-Vis) spectra were obtained by a UV-2450 UV-Vis spectrophotometer (Shimazu Co., Japan). Transmission electron microscopy (TEM) images were collected on a JEOL-1230 transmission electronic microscope (JEOL，Japan). Graphite oxide (JCNANO Co., China) was saved as carbon source. All other chemicals were of analytical grade. Milli-Q ultrapure water (Milli-pore, ≥18 MΩ·cm) was used throughout.

Experimental section

GQD Synthesis: 1.0 g GO powder was dispersed in 100 mL water. Two Pt sheets (4×4 cm^2) were saved as anode and cathode, which was fixed with a rubber plug to keep the distance between the two Pt sheets constant (3 cm). The constant voltage mode was used (15 V), and the synthesization current intensity varied in range of 50-30 mA/cm^2. Reacting for about 4 h at a suitable potential untill the black solution changed into dark-brown. As obtained solution was centrifuged (10000 r/min) to remove1the non-luminescence fraction with large size. Then dialyzed by dialysis bags (retained molecular weight: 7000, 3500 and 1000 Da) to obtained $GQD_{purple-blue}$, GQD_{blue} and GQD_{green}. The fraction of 1000-3500 Da for $GQD_{purple-blue}$, fraction of 3500-7000 Da for GQD_{blue} and fraction ＞7000 Da for GQD_{green}.

The procedure for the determination of the fluorescence quantum yields: Fluorescence (FL) quantum yields of the C-dots were obtained by using the comparative method of Williams et al.[1] The quantum yield of GQD, Φ_x, is calculated according to the following equation:

$$\Phi_x = \Phi_{std}\left(\frac{F_x}{F_{std}}\right)\left(\frac{A_{std}}{A_x}\right)\left(\frac{n_x}{n_{std}}\right)^2$$

Where Φ, F, A, and n are quantum yield of the standard sample, integrated photoluminescence intensity, absorbance, and refractive index, respectively. The subscript "std" refers to the standard fluorophore of known quantum yield, for an example, quinine sulfate used in present work. To minimize re-absorption effects, the absorbance of GQD and quinine sulfate solution in the 10 mm fluorescence cuvette were adjusted never exceed 0.1 at the excitation wavelength. The quinine sulfate was dissolved in 0.1 M H_2SO_4 (n_{std} was 1.33). The maximum excitation wavelengths of GQD and quinine sulfate solution are at ~390 nm and ~350 nm, respectively. We choose 360 nm as moderate excitation wavelength. The quantum yield of quinine bisulfate dissolved in 0.1 M H_2SO_4 is 0.54 reported in literature.[2] QY of as-prepared GQD was calculated according to the formulae above and summarized in Table S1

Detection of H_2O_2 and glucose: In H_2O_2 assay, GQD dispersed by NaAc buffer with a concentration of 50 μg/mL. 50 μL of GQD solution was added into 850 μL of NaAc buffer solution (pH: 4.0), followed by adding 50 μL of TMB solution (10 mg/mL in ethanol), then 50 μL NaAc buffer containing H_2O_2 with different concentration was added, then kept in 35 ^oC bath for 30 min before absorbance measurement. In glucose assay, 100 μL of 1 mg/mL GOx and 100 μL glucose of different concentrations in 200 μL phosphate buffer (PBS, 0.1 M, pH=7.0) were incubated at 37 °C for 30 min; 50 μL of TMB, 50 μL of GQD dispersion, and 800 μL of NaAc solution were added into 200 μL above glucose reaction solution; the mixed solution was incubated at 35 °C for 30 min and then for standard curve measurement. Repeat three times.

Table S1. QY of different GQDs.

sample	QY(%)
$GQD_{purple\text{-}blue}$	7.8±0.86
GQD_{blue}	5.9±1.20
GQD_{green}	3.1±1.54

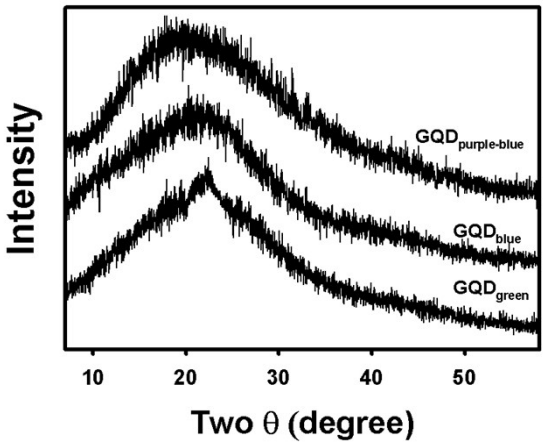

Figure S1 The typical X-ray diffraction (XRD) patterns of different GQDs.

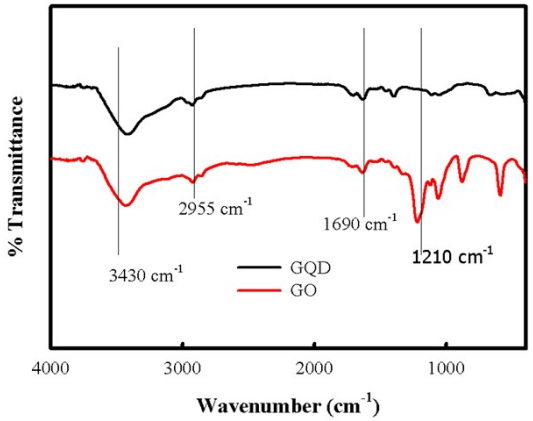

Figure S2 The FTIR spectra of GQD (black) and GO (red).

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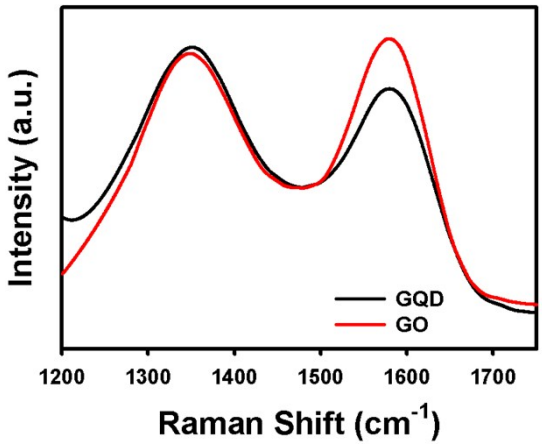

Figure S3 The Raman spectra of GQD (black) and GO (red).

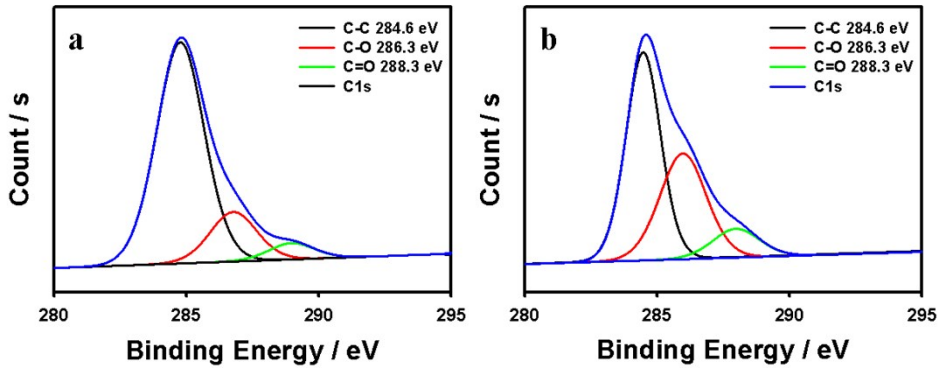

Figure S4 The XPS spectra of GO (a) and GQD (b).

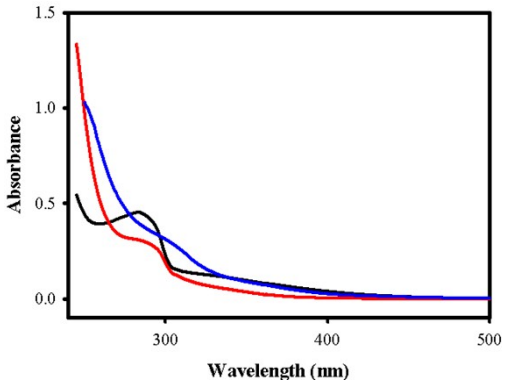

Figure S5 Absorbance of $GQD_{purple\text{-}blue}$ (black), GQD_{blue} (blue) and GQD_{green} (red), respectively. The concentration of GQDs were 50 μg/mL in water.

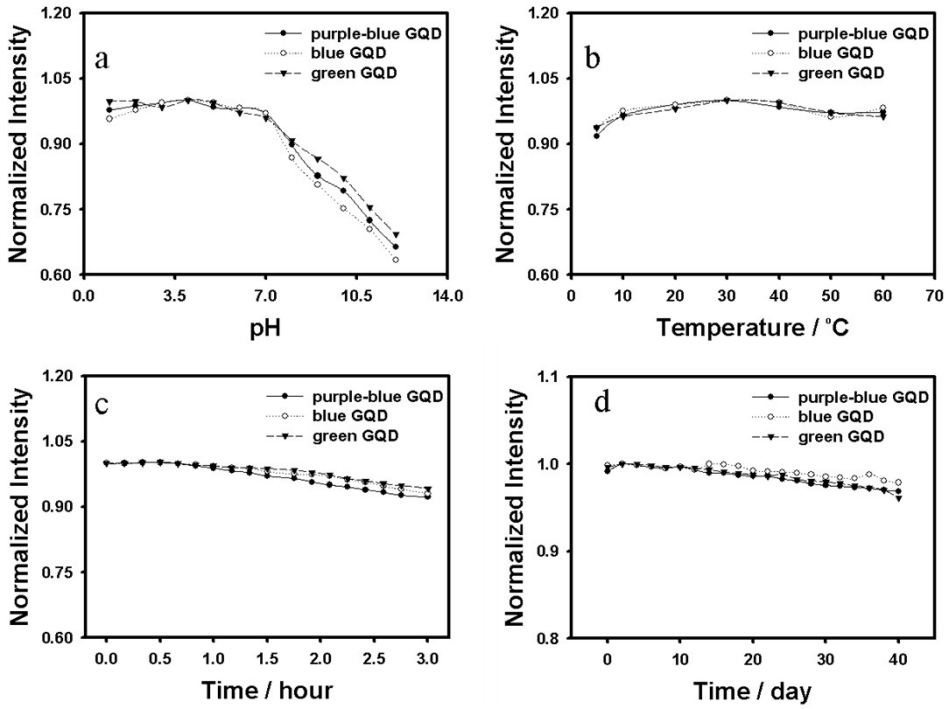

Figure S6 (a) The effect of pH value for the normalized FL intensity of different GQD solutions. (b) The normalized FL intensity of different GQD solutions at different temperature. The pH value was adjusted by 0.1 M H_2SO_4 and 0.1 M NaOH. The different GQD solutions were kept in room temperature. (c) Normalized emission intensity of different GQD solution during continuous excitation at 380, 400 and 420 nm. (d) The changes of normalized FL intensity of different GQD solution within a month.

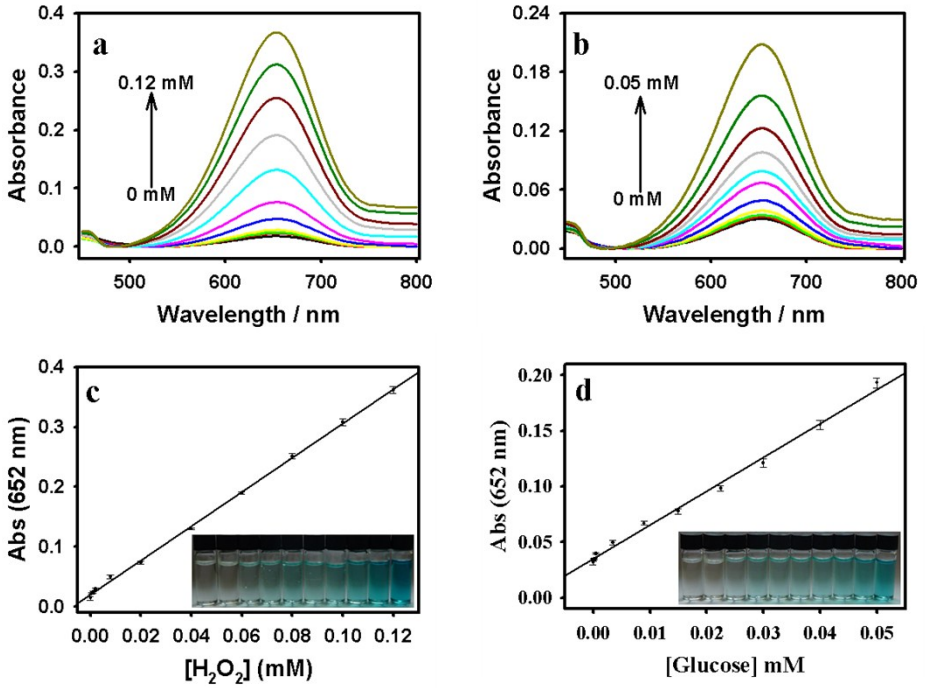

Figure S7 The absorbance spectra of TMB+GQD+H_2O_2 (a) and TMB+GQD+GOx+glucose (b) system with analyte of different concentration. Response curves of H_2O_2 (c) and glucose (d), respectively. Inset: images of production of colored products for different concentrations of H_2O_2 and glucose. The pH of NaAc buffer was 4.0. GQD of 2.5 μg/mL was used here. TMB was 0.5 mg/mL.

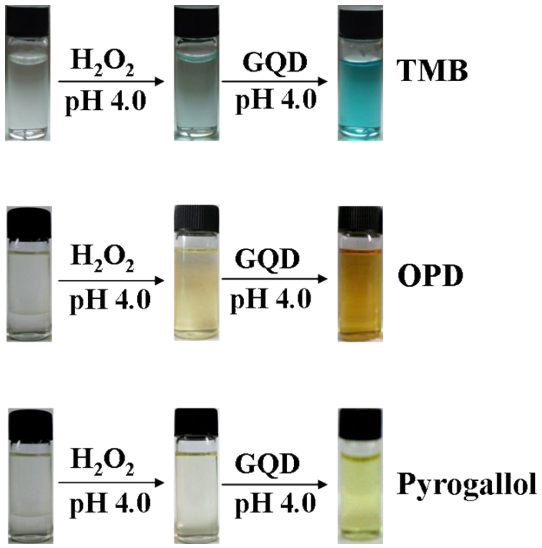

Figure S8 Images of oxidation color reaction of TMB, OPD, and pyrogallol by H_2O_2 after catalyzing by GQD at pH 4.0 NaAc buffer solution.

Reference

1. A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067-1071.
2. J. Deng, Q. Lu, N. Mi, H. Li, M. Liu, M. Xu, L. Tan, Q. Xie, Y. Zhang and S. Yao, *Chemistry – A European Journal*, 2014, **20**, 4993-4999.