

Electronic Supporting Information

for

Self-exothermic reaction prompted synthesis of single-layered graphene quantum dots at room temperature

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Materials and methods

Materials. Hydroquinone and triethylenetetramine (TETA) were commercially available from Aladdin Reagent Co., Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2) and Aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Kelong Chemical Group Co., Ltd. (Chengdu, China).

Characterization. The UV absorption spectral feature of s-GQDs was obtained from a Hitachi U-3010 spectrophotometer (Tokyo, Japan). The elemental composition of s-GQDs was measured with an ESCALAB 250 X-ray photoelectron spectroscopy. The FT-IR spectrum of s-GQDs was collected on a Hitachi FTIR-8400S Fourier Transform Infrared spectrometer (Tokyo, Japan). The HRTEM imaging of s-GQDs was performed on a Tecnai G2 F20 field emission transmission electron microscope (FEI, USA). The PL spectra of s-GQDs were recorded with a Hitachi F-2500 fluorescence spectrophotometer (Tokyo, Japan). Zeta potentials and hydrodynamic sizes of s-GQDs were measured using a ZEN3600 dynamic laser light scattering (DLS) (Malvern, English). The Raman spectrum of s-GQDs on the AgNPs solution was scanned through a LabRAM HR800 Laser confocal Raman spectrometer. The fluorescence lifetime of s-GQDs was measured with a FL-TCSPC fluorescence spectrophotometer (Horiba Jobin Yvon, France). The temperature of reaction solution was measured by a digital thermometer. The infrared thermal images were performed on a TiS40 Thermal Imager (Fluke, USA). The thermal effect of the self-exothermic reaction was measured through a differential scanning calorimeter (Netzsch, Germany).

Synthesis and purification of the s-GQDs. Hydroquinone (100 mg) was dissolved in 2.25 mL water, and then 2.5 mL H_2O_2 (20%) was added into the solution. Dark brown s-GQDs solution was observed within 5 min after the addition of 0.25 mL TETA at room temperature. Residual amounts of hydroquinone and TETA are removed through a cellulose ester dialysis membrane (500-1000 MWCO) over 48 h. The resulting material was dried by lyophilization, which were dispersed in water for further characterization and use.

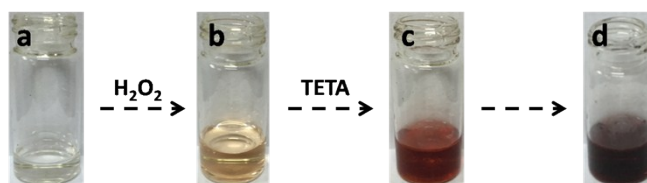


Fig. S1 Scheme of the synthesis process of the s-GQDs. (a) The hydroquinone solution; (b) the reaction solution after adding H_2O_2 ; (c) the resulting solution after adding TETA; (d) the final s-GQDs solution.

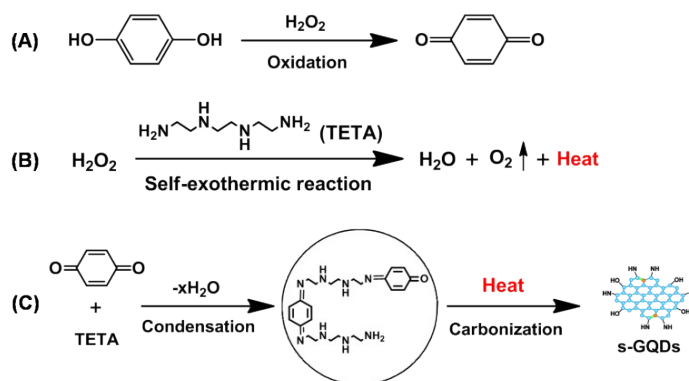


Fig. S2 Reaction process of the s-GQDs at room temperature.

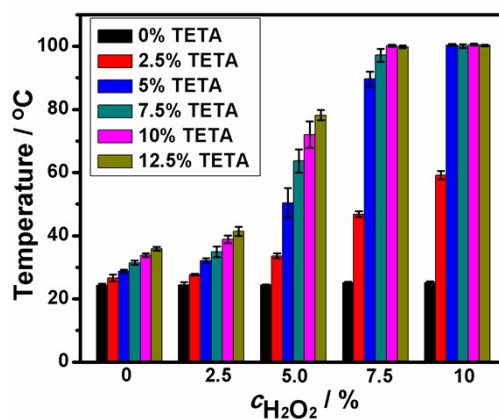


Fig. S3 Increased temperature of exothermic system in different mass fractions of H_2O_2 and volume fractions of TETA. Room temperature, 24.9 °C.

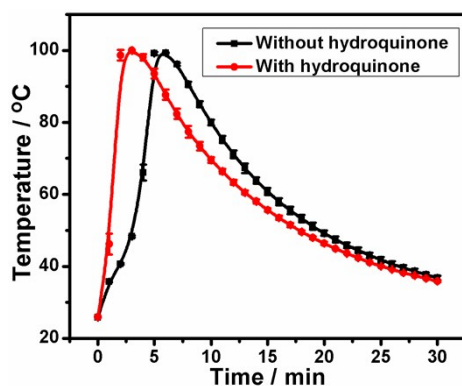


Fig. S4 The temperature change of self-exothermic system in the absence and presence of hydroquinone (100 mg) within 30 min. The mass fractions of H₂O₂ and volume fractions of TETA are 10% and 5%, respectively.

Table S1 The comparison of different synthesis methods with our approach.

Synthesis method	Reaction precursor	Oxidizing agent	T/°C	Time	Reference
Chemical breakdown	Carbon black	HNO ₃	/	24 h	1
Chemical breakdown	Carbon fibers	H ₂ SO ₄ and HNO ₃	80	26 h	2
Chemical breakdown	Graphene oxide	H ₂ SO ₄ and HNO ₃	250	34 h	3
Hydrothermal route	Citric acid and Tris-HMA	/	225	26 min	4
Hydrothermal route	Citric acid and dicyandiamide	/	180	3 h	5
Hydrothermal route	Citric acid and ammonia	/	200	3 h	6
Microwave synthesis	Graphene oxide	H ₂ SO ₄ and HNO ₃	/(240 W)	1-5 h	7
Self-exothermic reaction	Hydroquinone and TETA	/	Room temperature	5 min	This work

Table S2 The comparison of absolute quantum yield (QY) of s-GQDs (C-1) obtained in our experiment with GQDs (from C-2 to C-7) prepared by the common hydrothermal route. Hydroquinone: 100 mg; the volume fraction of TETA is 5%.

GQDs	T/°C	Time	Absolute QY/% (n=3)
C-1	Room temperature	5 min	2.30 ± 0.17
C-2	100	5 min	/
C-3	100	3 h	0.23 ± 0.06
C-4	150	5 min	/
C-5	150	3 h	1.27 ± 0.25
C-6	200	5 min	/
C-7	200	3 h	7.10 ± 0.95

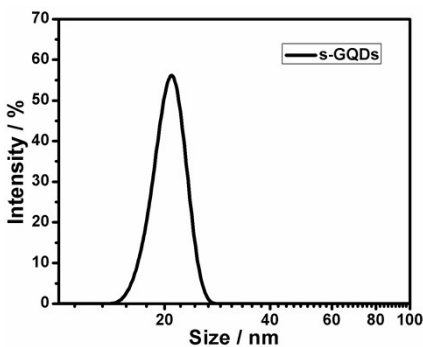


Fig. S5 The hydrodynamic size of the s-GQDs.

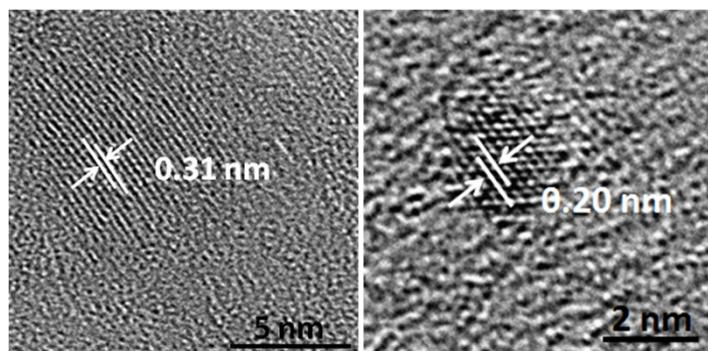


Fig. S6 The high-resolution TEM (HRTEM) images of the s-GQDs.

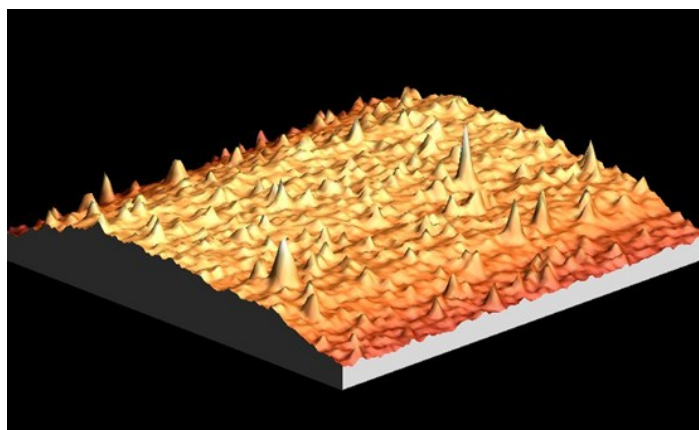


Fig. S7 The three-dimension AFM image of the s-GQDs.

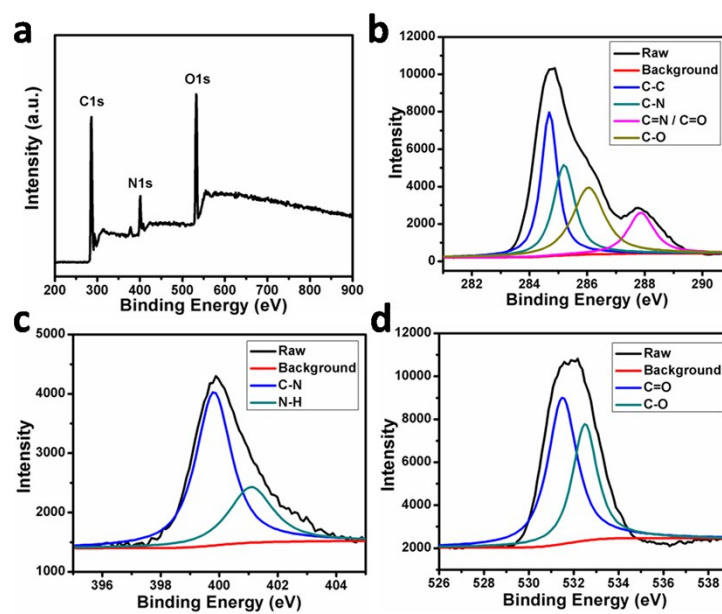


Fig. S8 The XPS spectra of the s-GQDs. (a) The XPS; (b) C1s; (c) N1s and (d) O1s spectra of s-GQDs.

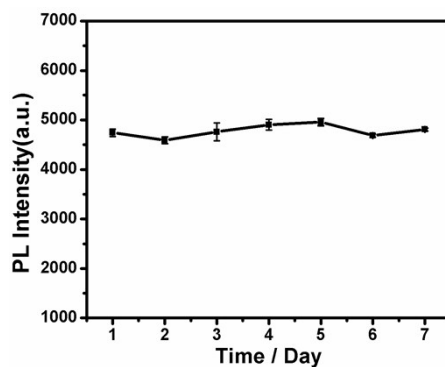


Fig. S9 The time-dependent colloidal stability of the s-GQDs. λ_{ex} : 330 nm; $c_{\text{s-GQDs}}$: 150 $\mu\text{g/mL}$.

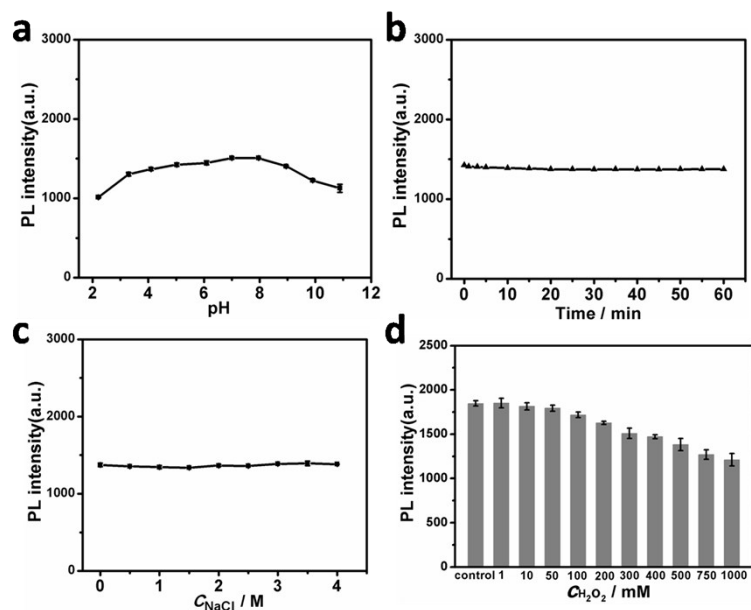


Fig. S10 The stability investigation of the s-GQDs. (a) The stability investigation in different BR buffer solution; (b) photostability; (c) the stability in a salty medium and (d) antioxidant capacity of s-GQDs. λ_{ex} : 330 nm; $c_{\text{s-GQDs}}$: 50 $\mu\text{g/mL}$.

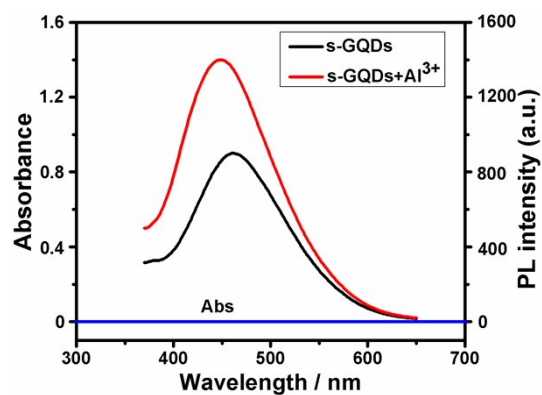


Fig. S11 The emission spectra of s-GQDs in the absence and presence of Al^{3+} and the UV absorption spectrum of Al^{3+} . pH, 5.4 ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer). $c_{\text{Al}^{3+}}$, 25 μM . $c_{\text{s-GQDs}}$, 25 $\mu\text{g/mL}$.

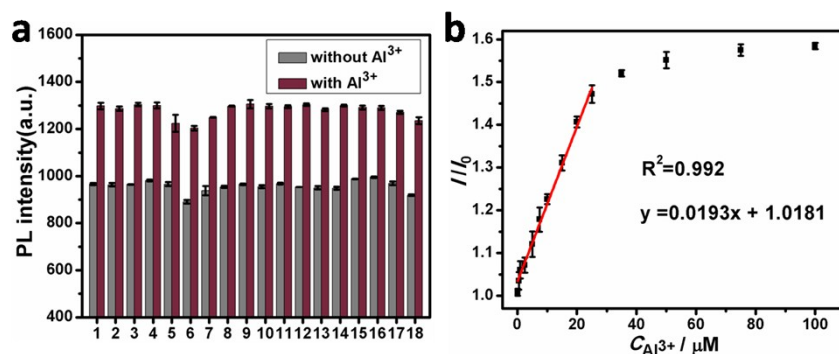


Fig. S12 The sensitivity and selectivity of Al³⁺ detection by using s-GQDs. (a) The selectivity of Al³⁺ detection. The columns represent: 1, control; 2, Ba²⁺; 3, Ca²⁺; 4, Cd²⁺; 5, Cr³⁺; 6, Fe³⁺; 7, Hg²⁺; 8, K⁺; 9, Li⁺; 10, Mg²⁺; 11, Mn²⁺; 12, Na⁺; 13, Ni²⁺; 14, Pb²⁺; 15, Zn²⁺; 16, Ag⁺; 17, Co²⁺; 18, Cu²⁺; Concentrations of all the metal ions and Al³⁺ are 25 μM and 20 μM, respectively. (b) The sensitivity of Al³⁺ detection. λ_{ex} : 330 nm; $c_{\text{s-GQDs}}$: 25 μg/mL; pH: 5.4 (CH₃COOH/CH₃COONa buffer).

Table S3 Determination of Al³⁺ in two kinds of water samples. pH: 5.4 (CH₃COOH/CH₃COONa buffer); λ_{ex} : 330 nm; $c_{\text{s-GQDs}}$: 25 μg/mL.

Add Al ³⁺ (μM)	Found (μM)	Recovery (%)	RSD (n=3, %)
Water sample 1 (tap water)			
1	1.03	102.8	0.3
10	10.10	101.0	1.5
20	20.51	102.6	0.7
Water sample 2 (lake water)			
1	1.10	109.9	3.3
10	9.30	93.0	2.2
20	20.77	103.9	1.4
Recovery (%) = 100 × (concentration found/concentration added)			

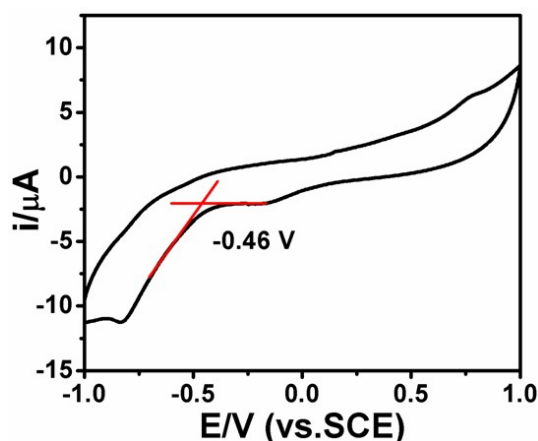


Fig. S13 Cyclic voltammograms of the s-GQDs in the solution state. The HOMO and LUMO energy levels of s-GQDs can be estimated according to the empirical formula:⁸

$$E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4)$$

$$E_{\text{LUMO}} = -e(E_{\text{red}} + 4.4)$$

Where E_{ox} and E_{red} are the onset of oxidation and reduction potential for s-GQDs, respectively. The E_{red} is determined to be -0.46 V. The corresponding E_{LUMO} is calculated to be -3.94 eV. However, the HOMO energy cannot be obtained due to the irreversible of the oxidation behavior. To determine the HOMO levels, we combine the E_{red} with the optical energy band gap (E_{g} , resulting from the absorption edge in the absorption spectrum):

$$E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}$$

E_{g} is estimated to be 4.01 eV. So, the E_{HOMO} is calculated to be -7.95 eV.

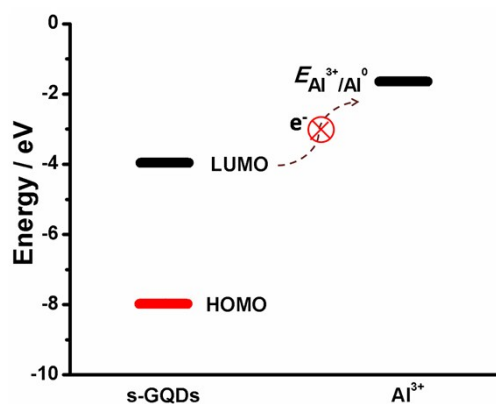


Fig. S14 The E_{LUMO} and E_{HOMO} of s-GQDs and oxidation-reduction potential of Al^{3+} .

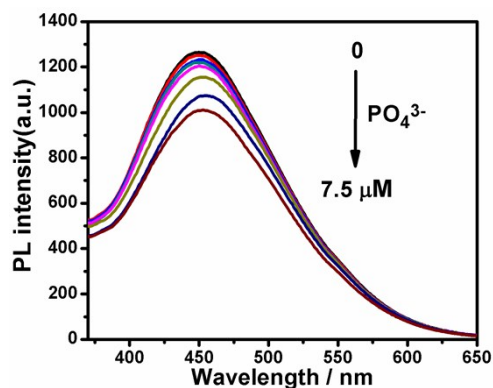


Fig. S15 The PL response of the s-GQDs-Al³⁺ mixture to PO₄³⁻ at varied concentrations. The concentration of PO₄³⁻ is 0, 0.25, 0.5, 0.75, 1, 2.5, 5, 7.5 μM, respectively; c_{Al³⁺}, 25 μM. λ_{ex}, 330 nm; c_{s-GQDs}, 25 μg/mL; pH, 5.4 (CH₃COOH/CH₃COONa buffer).

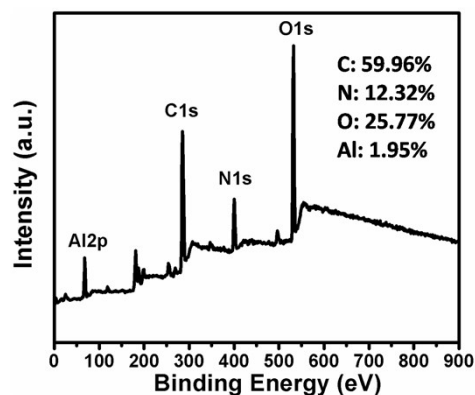


Fig. S16 The XPS spectrum of s-GQDs in the presence of Al³⁺. The s-GQDs mixed with Al³⁺ has been dialysis through a cellulose ester dialysis membrane (500-1000 MWCO) over 4 days before the determination of XPS.

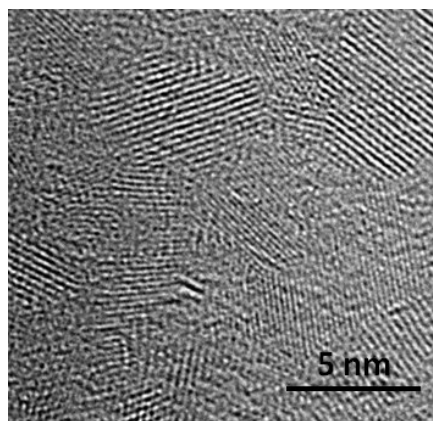


Fig. S17 HRTEM image of aggregated s-GQDs in the presence of Al³⁺.

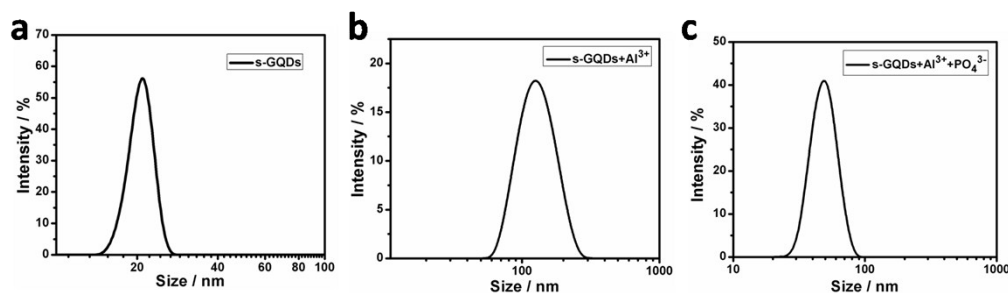


Fig. S18 The change of hydrodynamic size of the s-GQDs before and after adding into Al³⁺ (25 μM) and PO₄³⁻ (7.5 μM).

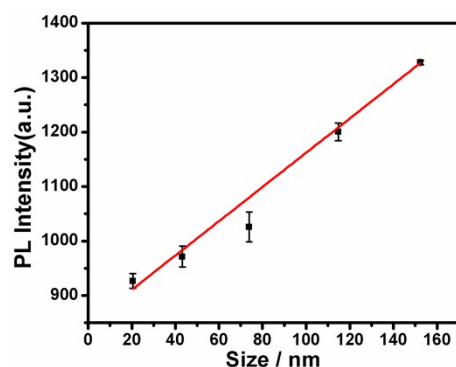


Fig. S19 The relationship between the PL intensity of the s-GQDs and the size of s-GQD-Al³⁺ in the presence of different concentrations of Al³⁺. The concentrations of Al³⁺ are 0, 1, 5, 15, 25 μM, respectively. λ_{ex}, 330 nm; pH, 5.4 (CH₃COOH/CH₃COONa buffer).

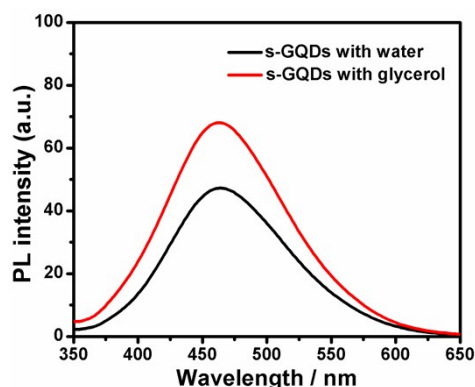


Fig. S20 The PL emission spectra of the s-GQDs in aqueous solution and 40 % glycerol solution. λ_{ex}: 330 nm; c_{s-GQDs}: 0.1 mg/mL.

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