Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information for:

High-yield Synthesis of Graphene Quantum Dots with Strong Green Photoluminescence

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Supplementary information

Experimental Section

Chemicals

D-(+)-glucose (≥99.5%), ethylenediamine (≥99.5%) and quinine sulfate (≥98.0%) were purchased from Sigma Aldrich. Hydrochloric acid (36.5-38.0wt. %) was supplied by Fisher Scientific. All chemicals were of analytical grade and used as received. DI-water used throughout all experiments was purified with a Millipore water system.

Synthesis of GQDs

GQDs were synthesized using glucose, ethylenediamine (EDA) and hydrochloric acid (HCl) as source materials. 1.0 g glucose, 400 μL EDA and 200 μL HCl were dissolved in 15 mL DI-water to form a transparent solution, which was then transferred into a 25 mL Teflon lined stainless steel autoclave and heated at 150-200 ºC for 3-6 h. After being cooled down, the as-received brown reaction solution was treated with further dialysis (the purification process was introduced as below) and vacuum drying to obtain the GQDs with a yield of ca. 60-70%. No strong acid treatment or further surface modification was needed in the synthesis process. The schematic representation of the growth mechanism of obtained GQDs is depicted in Figure S1.

Purification process

A "two-steps" purification process was employed to dialyse the as-received brown reaction solution by using two kinds of dialysis bags with molecular weight (Mw) of 3500 Da and 1000 Da in order to improve the purity of GQDs. The brown reaction solution was first dialysed for 5-8 h by using the dialysis bag with Mw of 3500 Da, and then the GQDs solution outside the dialysis bag with Mw of 3500 Da was dialysed again for 3-7 h by using the dialysis bag with Mw of 1000 Da. Finally, the GQDs solution inside the dialysis bag with Mw of 1000 Da was collected as the ultimate GQDs solution, which was used for the next investigation.

Characterizations

High-resolution transmission electron microscope (HRTEM) images were performed on JEM-2010F system operating at 200 kV. The specimens were prepared by drop-casting the sample

solution onto an ultrathin carbon coated copper grid, followed by drying at room temperature. The surface morphology and height distribution of obtained GQDs were measured by an atomic force microscopy (AFM, Dimension 3100) under ambient conditions. Fluorescence spectra of obtained GQDs were performed using a QuantaMaster™ 300 Plus Fluorescence Spectrofluorometer. The fluorescent images, green light emission, and the filters have been integrated in the fluorescence microscope. UV-Vis absorption spectrum was recorded using a Cary 100 UV-Visible spectrophotometer. Raman spectra of GQDs were measured by a Kaiser optical system (Ramanrxn™ Instrument) using a 785 nm laser. Fourier transform infrared (FTIR) spectra were taken on a Bruker IFS 55 FT-IR spectrophotometer. X-Ray photoelectron spectroscopy (XPS) data were recorded with a Kratos AXIS Ultra spectrometer with a monochromatized Al Ka X-ray source (1486.71 eV) for determining the compositions and chemical bonding configurations. Binding energy calibration was based on C1s at 284.5 eV.

QY measurements [1, 2]

Quinine sulfate (QS, 0.1 M H_2SO_4 as solvent; FL QY=54.0%) was chosen as the standard. The FL spectra, UV-Vis spectra of QS and obtained GQDs solutions with different concentrations were measured, respectively. Then FL QY of GQDs (in water) may be calculated according to the equation (1).

$$\phi_x = \phi_{st}(K_x / K_{st})(\eta_x / \eta_{st}) \quad (1)$$

where ϕ is the FL QY, K is the slope determined by the FL intensity vs. UV-Vis intensity curves and η is the refractive index of the solvent. The subscript "st" refers to a standard with known FL QY and "x" for the unknown samples. For these aqueous solutions, η_x / η_{st}=1. In order to minimize the re-absorption effects, absorption in the 10 mm FL cuvette was kept below 0.10 at the excitation wavelength.

Supplementary Figures

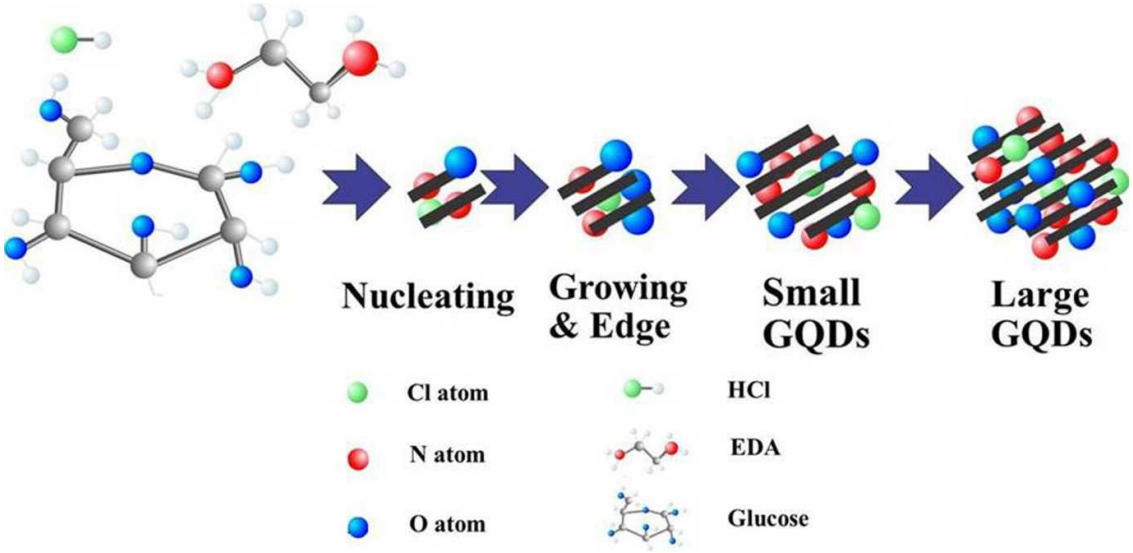

Figure S1 The growth mechanism of obtained GQDs

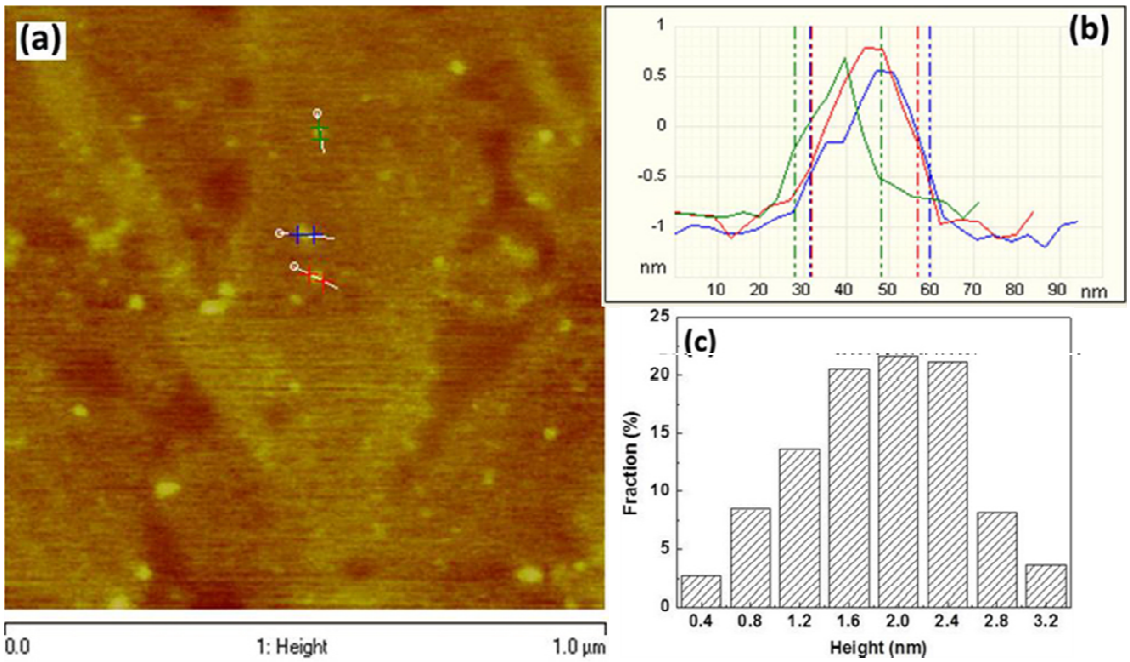

Figure S2 AFM images and height distribution of obtained GQDs.

(a), (b) AFM images; (c) Height distribution

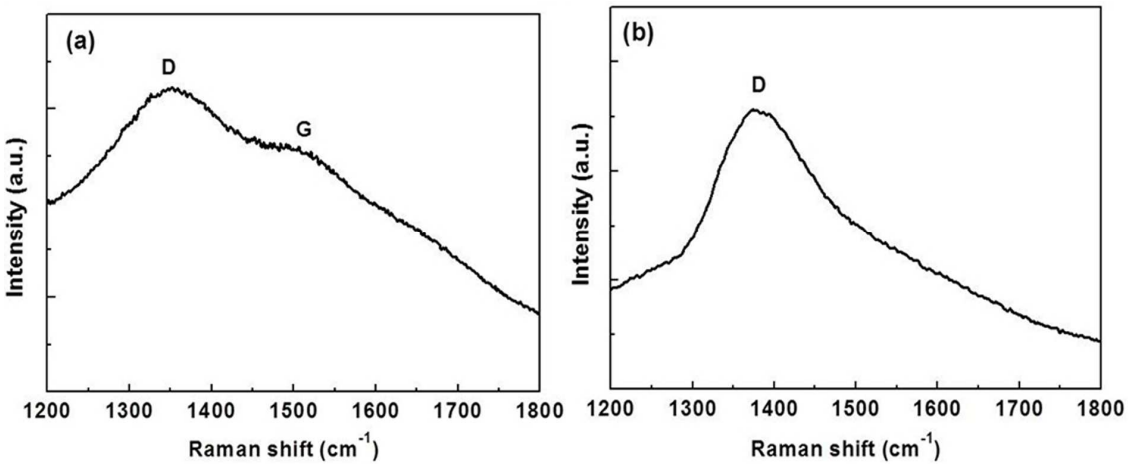

Figure S3 Raman spectra of GQDs. (a) GQDs in this work (44.3%, Table S3); (b) GQDs with higher FL QY (75.2%)

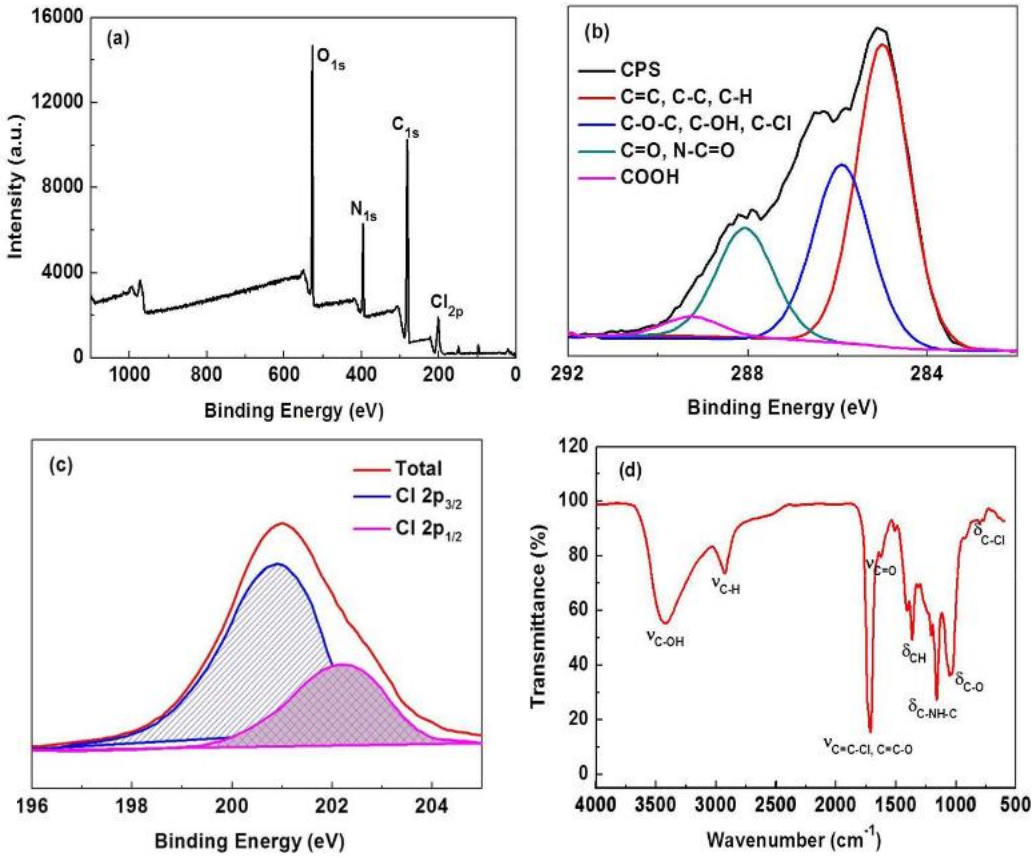

Figure S4 (a) Full-scan XPS spectrum; (b) C1s XPS spectrum; (c) Cl2p XPS spectrum; (d) FTIR spectrum of obtained GQDs

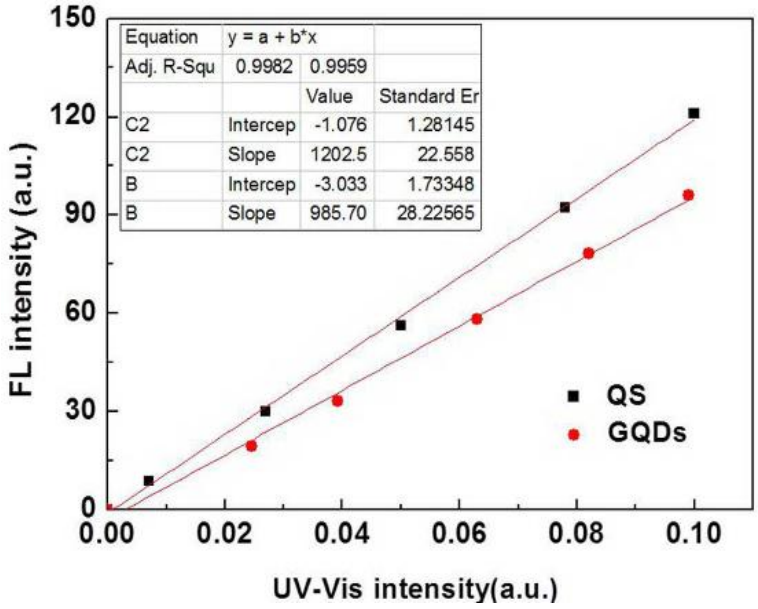

Figure S5 The plot of FL intensity with respect to UV-Vis intensity

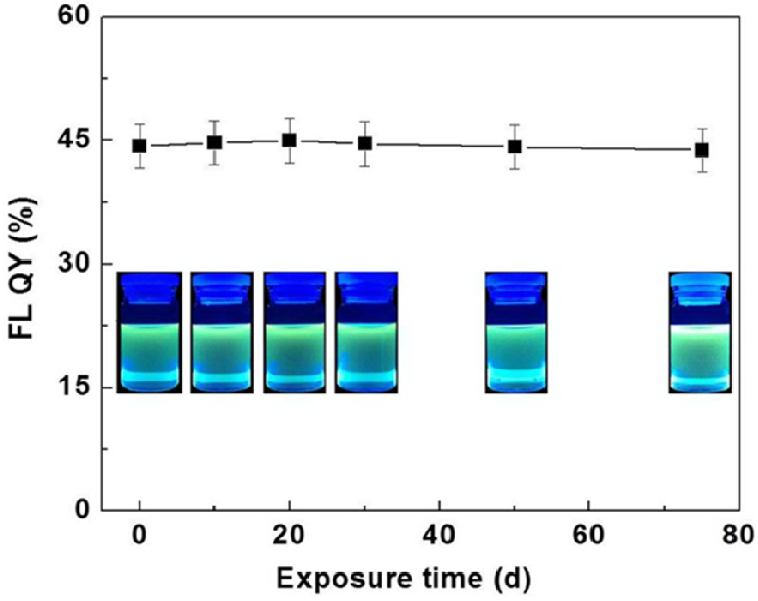

Figure S6 Effect of the exposure time under visible light on the green PL and FL QY of obtained GQDs

Figure S7 The solubility and PL of obtained GQDs in different solvents, and the solvents are acetone, DMF, glycerol, ethanol, PVA and DI-water in turn

Supplementary Tables

Table S1 The relative contents of various elements on the surface of obtained GQDs

Elements	Peak binding energy (eV)	Relative content (at. %)
C1s	284.75	57.2
O1s	286.15/288.15/289.15	23.4
N1s	288.15	14.6
Cl2p	286.15	5.8

Table S2 UV-Vis intensity, FL intensity of the GQDs aqueous solution and QS/0.1 M H_2SO_4 solution with different concentrations

Tested solutions	Concentration (M)	UV-Vis intensity (a.u.)	FL intensity (a.u.)
QS/0.1M H_2SO_4	7×10^{-8}	0.01	15.8
	1×10^{-7}	0.014	30.6
	3×10^{-7}	0.03	59.6
	5×10^{-7}	0.059	106.9
	7×10^{-7}	0.084	139.2
GQDs aqueous	7×10^{-8}	0.0245	19.4
	1×10^{-7}	0.0392	33.1
	3×10^{-7}	0.063	58.2
	5×10^{-7}	0.082	78.3
	7×10^{-7}	0.099	96.1

Table S3 FL QY of obtained GQDs

Serial	QS	GQDs
K	1202.51	985.70
R^2	0.9982	0.9959
ϕ (%)	54.0	44.3

Supplementary References

1 S. J. Zhuo, M. W. Shao and S. T. Lee, *ACS Nano*, 2012, **6**, 1059.

2 Z. H. Wang, J. F. Xia, C. F. Zhou, B. Via, Y. Z. Xia, F. F. Zhang, Y. H. Li, L. H. Xia and J. Tang, *Col. Surf. B: Biointerfaces*, 2013, **112**, 192.