Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Separating Graphene Quantum Dots by Lateral Size through Gel Column Chromatography

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Experimental Section

Preparation and Separation of GQDs

The raw GQDs by a photon-Fenton reaction were prepared according to our previous work,[1] followed by concentration, dialysis and freeze-drying. In order to avoid the loss of small size GQDs, a kind of 100-500 Da (retained molecular weight) dialysis bag was used to remove the salts. Then, the freeze-drying GQDs were formulated into 2 mg ml^{-1} GQDs, and 4 ml suspension at this concentration was added slowly into the column of Sephadex G25 gel from its top. When the Sephadex G25 gel column was almost completely submerged by GQDs solution, the deionized water was slowly added into the column from its top by a peristaltic pump at a speed of 1 ml/min. Then the solution from the bottom of the gel column was collected (1.5 ml each time), and the samples were named as GQDs 1-8 according to the collection order.

Fabrication of Organic Solar Cells (OSCs)

To prepare zinc oxide (ZnO) precursor solution, 0.5 mmol zinc acetate and monoethanolamine were added into 10 ml 2-methoxy ethanol. The mixture solution was stirred at 60 °C for 2 hr to yield a homogeneous sol.[2] Inverted hybrid solar cells were fabricated to study the photoelectric property of GQDs. Firstly, the Indium Tin Oxide (ITO) coated glass substrates were sequentially ultrasonic cleaned with detergent, ultrapure water acetone, isopropyl alcohol and dried with nitrogen gun. Secondly, the ITO coated glass substrates were pretreated on a hot plate at 100 °C for 8 h, and spin coated ZnO film by the ZnO precursor solution at 3000 rpm for 30 s followed with annealing at 100 °C for 16 hr.[3] Thirdly, the active layer was fabricated by spin-coating the polymer DCB solution with P3HT (20 mg mL^{-1}), PCBM(16 mg mL^{-1}) and GQDs (0.2 mg mL^{-1}) on the ZnO film at 800 rpm for 40s, and two different GQDs were chose to be compared. The samples were then transfered to a covered Petri dish in the air and were slowly dried. Fourthly, 6 nm MoO_3 and 120 nm Ag layers were evaporated onto the active layer under about 3×10^{-6} Torr, the deposition rates were 0.5 and 2 nm/s respectively. Finally, devices were annealed at 150 °C for 15 min after the evaporation.[4, 5] The solar cell fabrication was a nitrogen glove box free process.

Measurement

The morphologies and sizes of the sorted GQDs were characterized by JEM-2100F transmission electron microscope (TEM, JEOL, Japan) and atomic force microscopy (AFM, Bruker, USA). The sample was prepared by dropping the aqueous suspension of GQDs on a copper grid with trathin carbon film for TEM, and on a freshly cleaved mica surface and drying on a hot plate at 70 ℃ for AFM images. The fluorescence of the samples was measured under 302 nm UV light, which was recorded by optical camera. The photoluminescence (PL) spectra of the GQDs were acquired with a Cary Eclipse spectrofluorometer (Varian, USA). The UV−vis absorptions of GQDs were measured with a Shimadzu UV-2550 (Shimadzu, Japan) spectrophotometer. A Keithley 2401 Source Measurement Unit was chose for measuring the current density-voltage (J-V) characteristics of the solar cell in the air under Air Mass 1.5 Global (AM 1.5 G) irradiation (100mW/cm^2) with a solar simulator.

Quantum Yield (QY) Measurements:

The PL quantum yields of GQDs were calculated with quinine sulfate as a standard (QY = 0.577) according to the follow formula, which was reported in the literature.[6, 7]

$$\Phi = \Phi_s(I/I_s)(A/A_s)(n_s/n)^2$$

Where Φ and I represent the quantum yield and the measured integrated emission intensity respectively, and A and n represent the optical density and the refractive index of the solvent (1.33 for water) respectively. The subscript "s" refers to the standard of known quantum yield of quinine sulfate. In order to reduce the re-absorption effects, the absorption of the 10 mm fluorescence cuvette was kept under 0.05 at the excitation wavelength (340 nm).

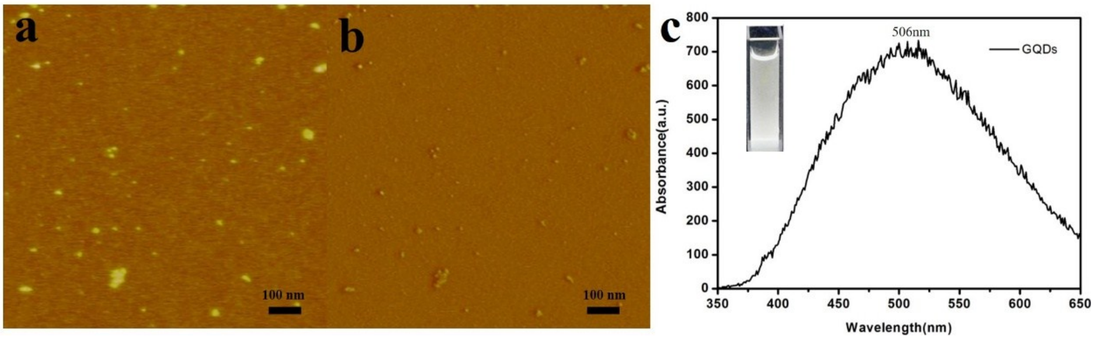

Figure S1 Taping mode AFM height (a) and phase (b) images of as-prepared GQDs,(c) the PL spectrogram of as-prepared GQDs, and the inset is the fluorescence photo of the as-prepared GQDs under 302 nm ultraviolet lamp.

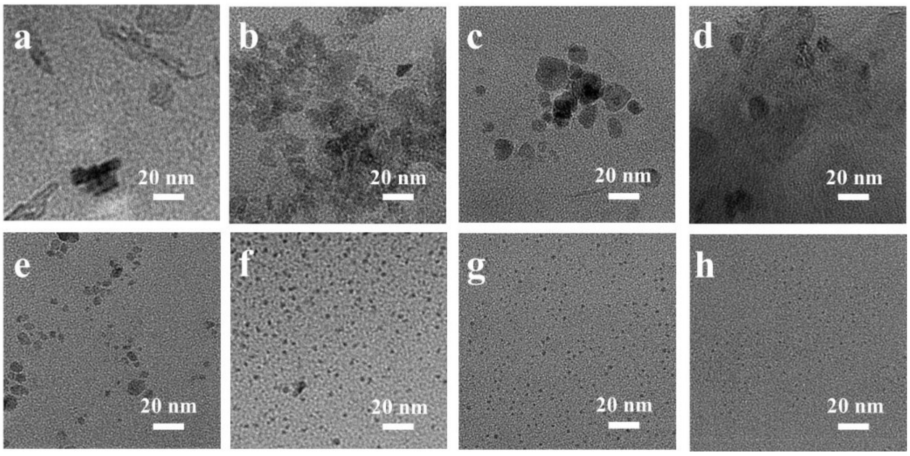

Figure S2 TEM images of the separated GQDs samples, in turn is the sample of (a) GQDs 1, (b) GQDs 2, (c) GQDs 3, (d) GQDs 4, (e) GQDs 5, (f) GQDs 6, (g) GQDs 7, (h) GQDs 8.

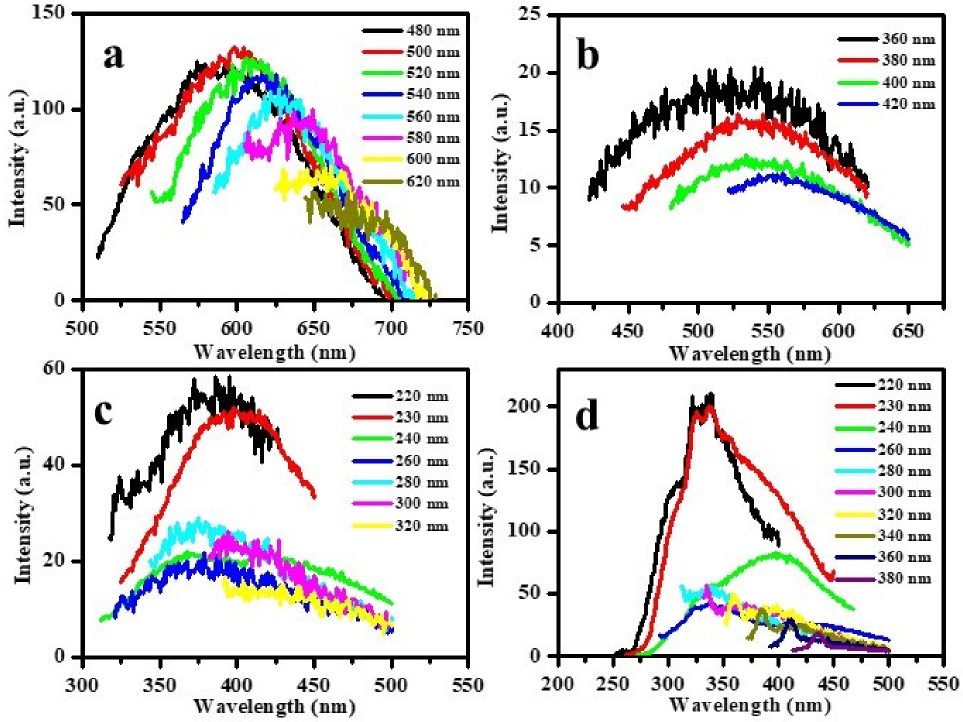

Figure S3(a) the emission spectra of GQDs-1/red at different excitation wavelengths from 480 nm to 620 nm; (b) the emission spectra of GQDs-2/orange at different excitation wavelengths from 360 nm to 420 nm; (c) the emission spectra of GQDs-7/blue at different excitation wavelengths from 220 nm to 320 nm; (d) the emission spectra of GQDs-8/purple at different excitation wavelengths from 220 nm to 380 nm.

Figure S4 The bottom row is the photo of the GQDs aqueous suspension prepared via the photo-fenton reaction with different time under daylight lamp; the top row is the corresponding fluorescence photo under UV irradiation (302 nm).

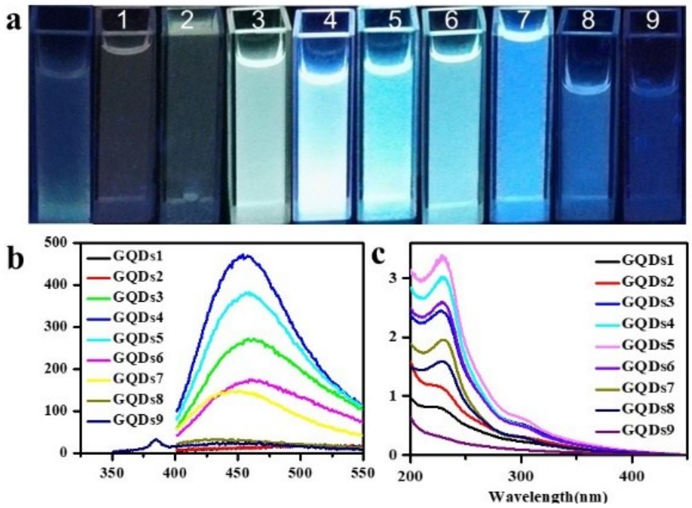

Figure S5 (a) the fluorescence photos of as-prepared GQDs-90 mins and the collected GQDs aqueous suspension under UV irradiation (302 nm); the corresponding PL spectra (b) and UV–vis absorption spectra (c) using the GQDs-90min as raw material via gel column chromatography.

Table S1 PL quantum yields of the separated GQDs using quinine sulfate as a reference.

GQDs	Abs.at 340 nm(A)	Integrated emission intensity (I)	Refractive index of solvent (n)	Quantum Yield (QY)
GQDs-1/red	0.02055	290	1.33	0.611%
GQDs-2/orange	0.034894	610.1	1.33	0.758%
GQDs-3/yellow	0.027029	1617.2	1.33	2.592%
GQDs-4/green	0.04199	5722.9	1.33	5.905%
GQDs-5/cyan	0.015187	636.4	1.33	1.816%
GQDs-6/light blue	0.025357	284.7	1.33	0.486%
GQDs-7/blue	0.045294	271.1	1.33	0.259%
GQDs-8/purple	0.005404	24.8	1.33	0.199%
As-prepared	0.03971	904	1.33	0.99%

Table S2 Performance details (V_{oc}, J_{sc}, FF and PCE) of ternary hybrid solar cells based on different GQDs under simulated AM 1.5G 100 mW illumination.

GQDs	J_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	PCE (%)
None	9.78	0.60	52.13	3.07
As-prepared GQDs	10.50	0.61	53.69	3.46
GQDs-4/green	11.50	0.60	56.03	3.91

References

1. X. Zhou, Y. Zhang, C. Wang, X. Wu, Y. Yang, B. Zheng, H. Wu, S. Guo and J. Zhang, *ACS Nano*, 2012, **6**, 6592-6599.
2. Z. Q. Liang, Q. F. Zhang, O. Wiranwetchayan, J. T. Xi, Z. Yang, K. Park, C. D. Li and G. Z. Cao, *Advanced Functional Materials*, 2012, **22**, 2194-2201.
3. X. Bao, A. Yang, Y. Yang, T. Wang, L. Sun, N. Wang and L. Han, *Physica B: Condensed Matter*, 2014, **432**, 1-4.
4. M. S. White, D. C. Olson, S. E. Shaheen, N. Kopidakis and D. S. Ginley, *Applied Physics Letters*, 2006, **89**, 143517.
5. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nature materials*, 2005, **4**, 864-868.
6. H. Sun, N. Gao, L. Wu, J. Ren, W. Wei and X. Qu, *Chemistry*, 2013, **19**, 13362-13368.
7. H. Sun, L. Wu, N. Gao, J. Ren and X. Qu, *ACS applied materials & interfaces*, 2013, **5**, 1174-1179.