Electronic Supplementary Information

For

Preparation of graphene oxide and polymer-like quantum dots and their one- and two-photon induced fluorescence properties

Jia Jia Huang,[ab] Min Zhi Rong*[b] and Ming Qiu Zhang*[b]

[a]*School of Chemical Engineering and Energy, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China*
[b]*Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, GD HPPC Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China*
E-mail: cesrmz@mail.sysu.edu.cn; cesrmz@mail.sysu.edu.cn

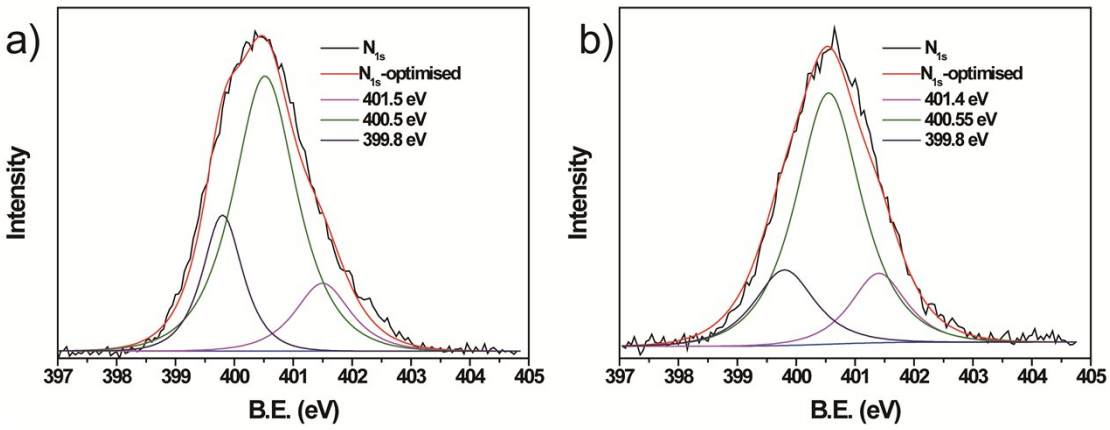

Fig.S1 XPS spectra of N1s of PQDs (a) and GOQDs (b)

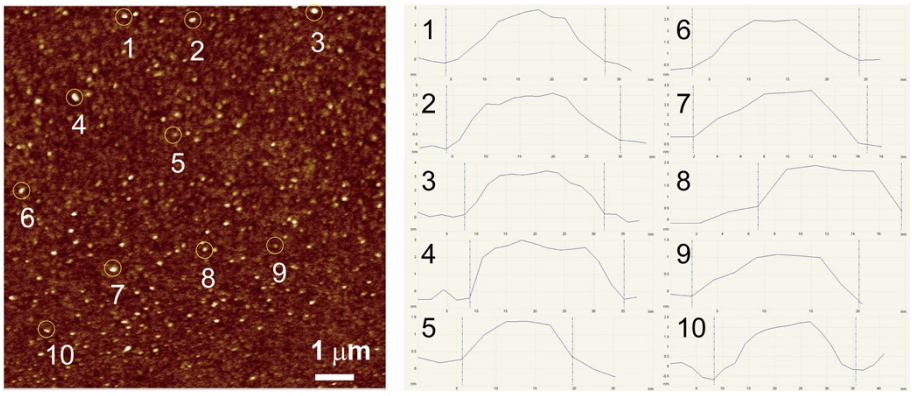

Fig. S2 Height profiles of ten random GOQDs.

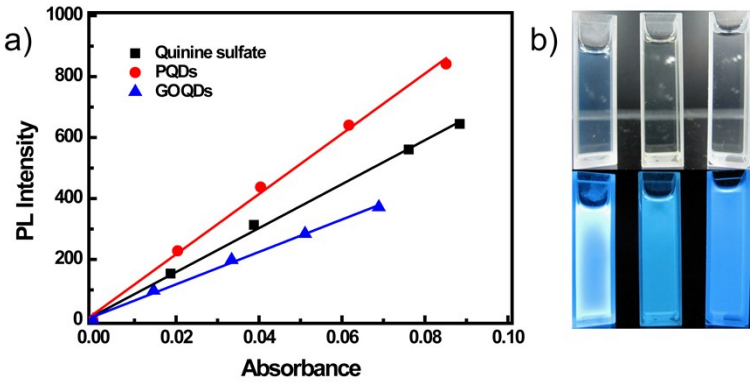

Fig. S3 (a) Integrated PL intensity versus absorbance plot of PQDs, GOQDs and quinine sulphate. (b) Photographs of PQDs, GOQDs and quinine sulfate (from left to right, 10 μg/ml) under daylight (up) and 365 nm UV (down).

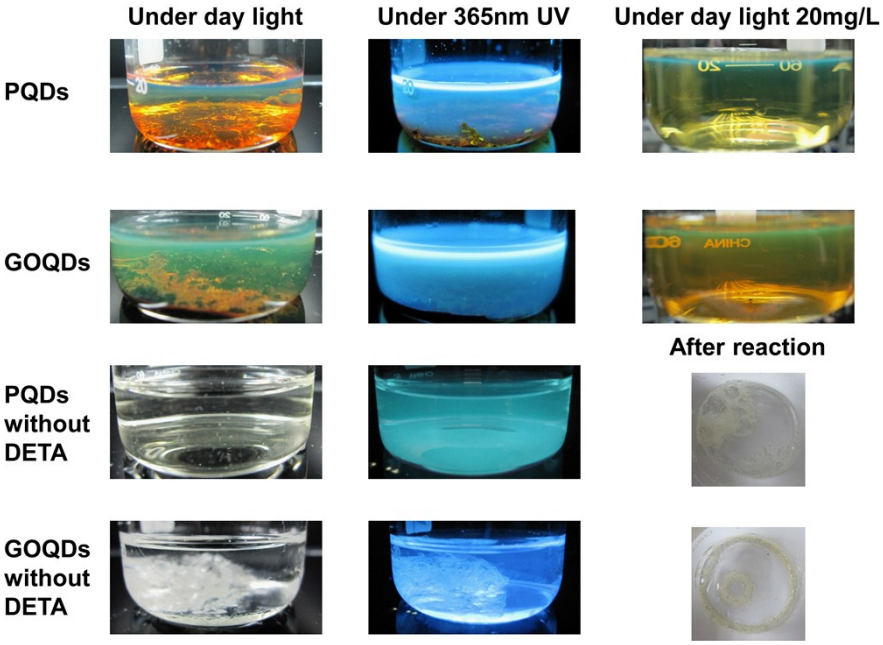

Fig. S4 Photographs of PQDs and GOQDs with and without DETA under daylight and 365 nm UV.

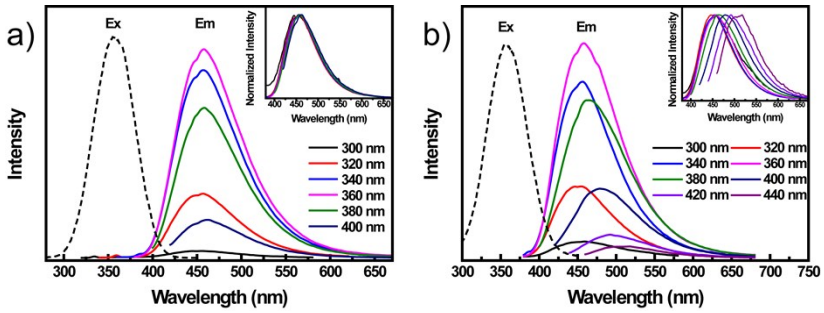

Fig. S5 Excitation and emission spectra of (a) PQDs and (b) GOQDs aqueous solution

(10 μg/ml) at different excitation wavelengths. Inset: normalized emission spectra.

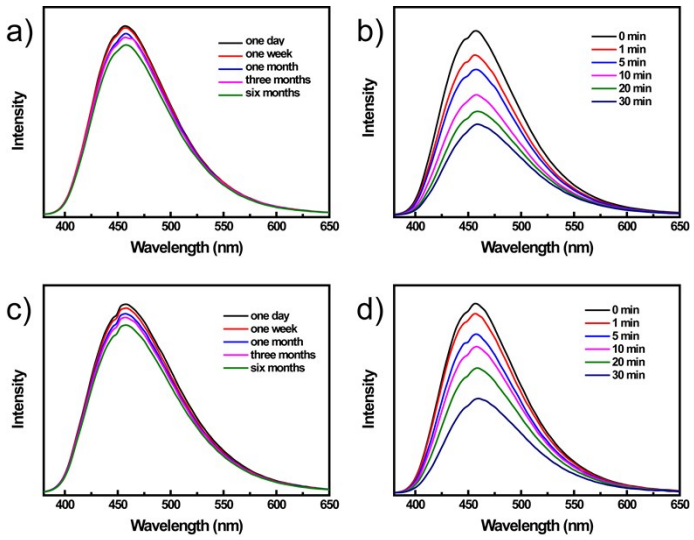

Fig. S6 PL spectra of (a, b) PQDs and (c, d) GOQDs in aqueous solution (a, c) after different storage times and (b, d) after exposure to 500 W UV light for different times. PQDs and GOQDs: 10 μg/ml; excitation wavelength: 360 nm.

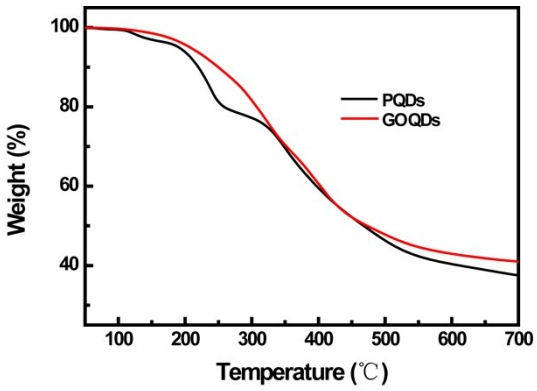

Fig. S7 TGA curves of PQDs and GOQDs.

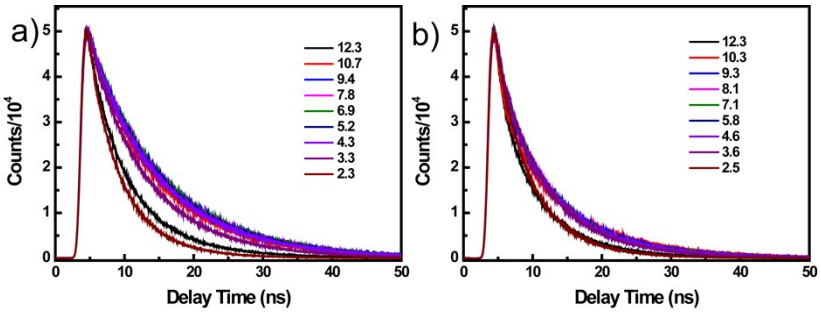

Fig. S8 Fluorescence life time decay profiles of (a) PQDs and (b) GOQDs aqueous

solution (10 μg/ml) at different pH values with excitation at 405 nm. The emission was monitored at 460 nm.

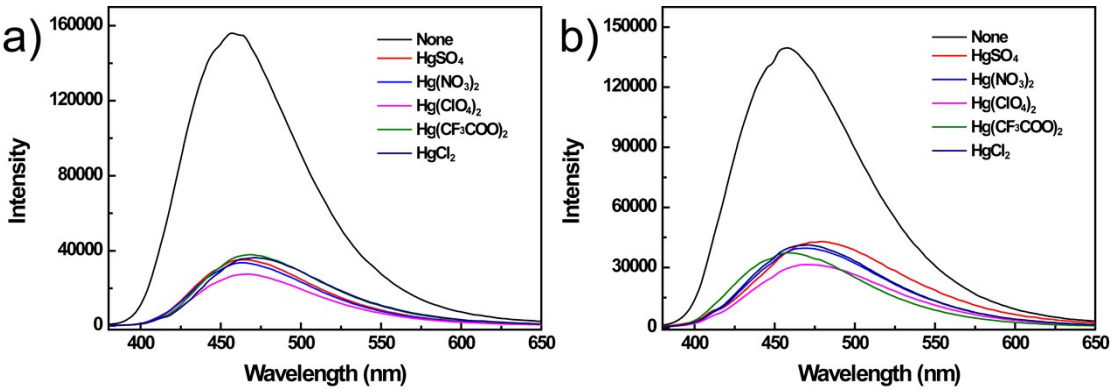

Fig. S9 Effect of different mercury salts (0.05 mM) on the PL intensity of (a) PQDs and (b)GOQDs (1 μg/ml) with the excitation wavelength at 360 nm.

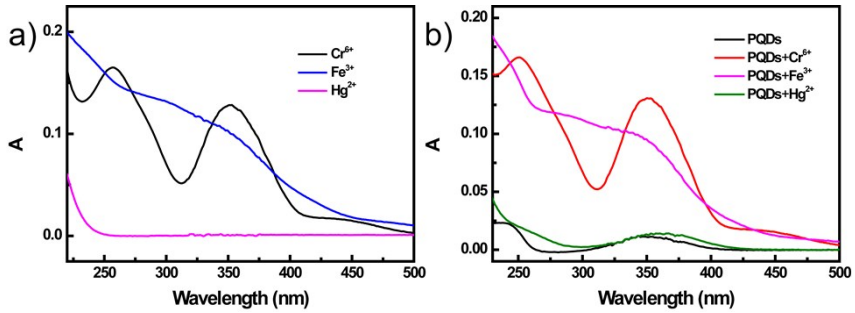

Fig. S10 (a) UV-vis absorption spectra of Cr^{6+}, Fe^{3+} and Hg^{2+}. (b) UV-vis absorption spectra of PQDs and their mixture with Cr^{6+}, Fe^{3+} and Hg^{2+}. PQDs: 1 μg/ml; Cr^{6+}, Fe^{3+} and Hg^{2+}: 0.05 mM.

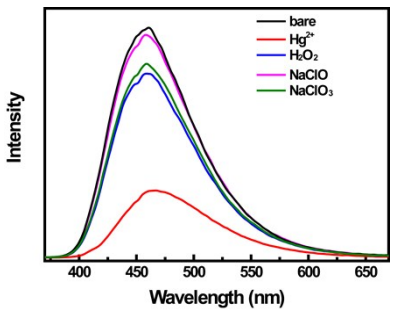

Fig. S11 Effect of oxidant (0.05 mM) and Hg^{2+} (0.05 mM) on the PL intensity of GOQDs (1 μg/ml) with the excitation wavelength at 360 nm.

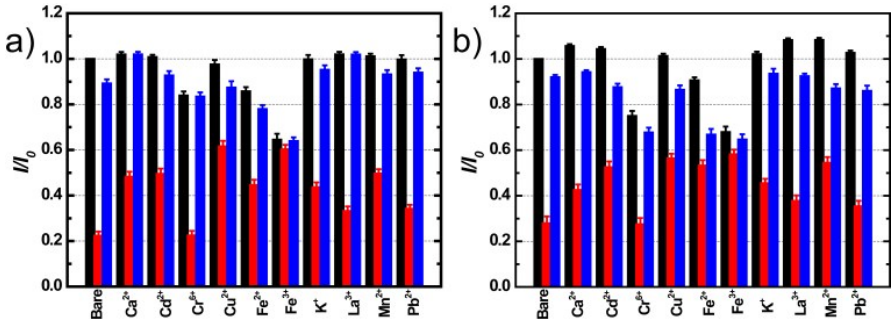

Fig. S12 Relative PL intensity (I/I_o) of (a) PQDs and (b) GOQDs aqueous solution (1 μg/ml) containing various metal ions (50 μM) without (black) and with Hg^{2+} (red), after the addition of 100 μM EDTA (blue).

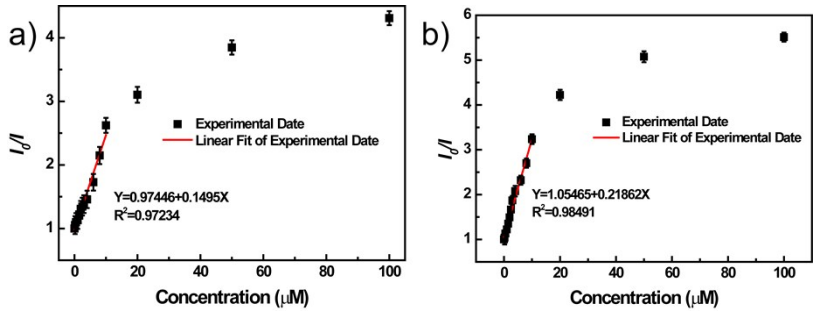

Fig. S13 Plots of PL intensity ratio of (a) PQDs and (b) GOQDs aqueous solution (1 μg/ml) at 460 nm versus Hg^{2+} concentration (excited at 360 nm). I_0 and I correspond to the PL intensities of PQDs or GOQDs at 460 nm in the absence and presence of Hg^{2+}, respectively.

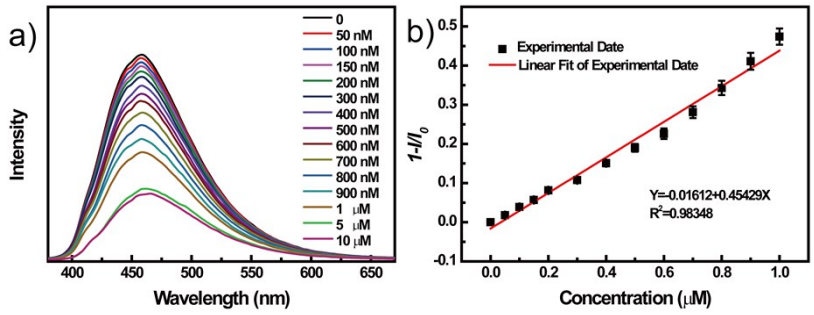

Fig. S14 (a) PL spectra of PQDs aqueous solution (0.1 μg/ml) with different Hg^{2+} concentrations (excited at 360 nm). (b) Plot of PL intensity ratio of PQDs aqueous solution (0.1 μg/ml) at 460 nm versus Hg^{2+} concentrations in the range from 0 to 1.0 μM.

Table S1 Elemental analysis of CA, PQDs and GOQDs

Sample	C (wt%)	H (wt%)	N (wt %)	O (wt%, calculated)	C/N	C/O
CA	37.5	4.17	0	58.33		0.86
PQDs	46.70	5.52	12.77	35.01	4.27	1.78
GOQDs	52.70	6.16	11.76	29.38	5.23	2.39

Table S2 XPS analysis of PQDs and GOQDs

Sample	C (%)	O (%)	N (%)	C=C/C-C (%)	Oxidized carbon (%)	Nitrous carbon (%)
PQDs	57.8	27.4	14.8	27.8	44.8	27.4
GOQDs	63.1	23.7	13.2	31.6	40.7	27.7

Table S3 Time-resolved fluorescence-delay analysis of PQDs at different pH values

pH	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ (ns)	χ^2
2.3	3.3	40	6.2	60	5.5	1.2
3.3	4.6	15	9.4	85	9.0	1.4
4.3	3.7	5	10.6	95	10.5	1.5
5.2	3.6	5	10.9	95	10.8	1.6
6.9	2.9	2	10.9	98	10.8	1.7
7.8	3.2	3	10.9	97	10.8	1.7
9.4	3.4	3	10.9	97	10.8	1.6
10.7	3.4	5	10.2	95	10.1	1.6
12.3	4.0	45	8.7	55	7.4	1.6

Table S4 Time-resolved fluorescence-delay analysis of GOQDs at different pH values

pH	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ (ns)	χ^2
2.5	3.0	28	6.3	72	5.8	1.3
3.5	3.0	17	8.2	83	7.9	1.5
4.6	2.9	18	9.0	82	8.5	1.2
5.8	3.2	20	8.8	80	8.4	1.2
7.1	3.0	19	9.0	81	8.6	1.3
8.1	3.0	19	9.0	81	8.5	1.2
9.3	2.8	20	8.5	80	8.1	1.7
10.3	2.6	20	8.2	80	7.7	1.2
12.3	2.0	22	7.2	78	6.8	1.1

Table S5 Formation constants for metal complexes with EDTA

Metal ions	lg k	Metal ions	lg k
Na^+	1.7	Cd^{2+}	16.5
Ca^{2+}	10.7	Pb^{2+}	18.0
Mn^{2+}	13.9	Cu^{2+}	18.8
Fe^{2+}	14.3	Hg^{2+}	21.8
La^{3+}	15.4	Fe^{3+}	25.1

Table S6 Time-resolved fluorescence-delay analysis of PQDs with different [Hg^{2+}]

[Hg^{2+}]/μM	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ (ns)	χ^2
0	5.1	2	15.4	98	15.3	1.14
1	4.7	23	15.2	77	14.3	1.17
4	4.4	32	14.9	68	13.6	1.16
20	4.6	63	14.3	37	10.9	1.29
100	4.4	75	13.4	25	9.0	1.23

Table S7 Time-resolved fluorescence-delay analysis of GOQDs with different $[Hg^{2+}]$

$[Hg^{2+}]$/μM	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ (ns)	χ^2
0	4.6	18	12.4	82	11.8	1.24
1	4.8	21	12.1	79	11.4	1.22
4	4.9	25	11.9	75	11.1	1.24
20	4.6	37	10.9	63	9.6	1.24
100	4.2	36	9.8	64	8.7	1.21

Table S8 Potentials of the elements at 25 °C

Half-reaction	Standard potential	Half-reaction	Standard potential
$Fe^{3+}+e^-\rightarrow Fe^{2+}$	0.771	$Ca^{2+}+2e^-\rightarrow Ca$	-2.868
$Fe^{3+}+3e^-\rightarrow Fe$	-0.037	$Cu^{2+}+2e^-\rightarrow Cu$	0.3419
$Fe^{2+}+e^-\rightarrow Fe$	-0.477	$Mn^{2+}+2e^-\rightarrow Mn$	-1.185
$2Hg^{2+}+2e^-\rightarrow Hg_2^{2+}$	0.920	$Pb^{2+}+2e^-\rightarrow Pb$	-1.262
$Hg^{2+}+2e^-\rightarrow Hg$	0.851	$Cd^{2+}+2e^-\rightarrow Cd$	-0.403
$Hg_2^{2+}+2e^-\rightarrow 2Hg$	0.7973	$La^{3+}+3e^-\rightarrow La$	-2.522