Supporting Information

Gamma Ray Shifted and Enhanced Photoluminescence of Graphene

Quantum Dots

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1. Experimental Section

1.1. Materials.

Graphene was purchased from Nanjing XFNano Materials Technology Company. Pyrene was purchased from J&K Chemical Science and Technology Ltd. Other reagents were of analytical reagent grade and were used without further purification. Double-distilled water was used throughout the work.

1.2. Synthesis of GQD-OH, GQD-NH₂ and m-GQDs.

GQD-OH, GQD-NH₂, and m-GQDs were synthesized by modifying a previously reported method.²² Briefly, 1,3,6-trinitropyrene (Figure S1b) was obtained through filtering the nitration production of pyrene (Figure S1a) under refluxing and stirring in HNO₃ at 80 °C for 12 h. 0.15 g trinitropyrene was dispersed in 0.2 M NaOH solution (35 mL) by ultrasonication for 2 h. The suspension was transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 10 h. After cooling to room temperature, the suspension was filtered through 0.22 μ m microporous membrane to remove the insoluble products. The filtrate was dialyzed in a dialysis bag (retained molecular weight: 3500 Da) and the GQD-OH were obtained. The synthetic process of GQD-NH₂ and m-GQD were similar to that of the GQD-OH except for the substitution of NaOH solution with 1.2 M ammonia or the mixed solution containing 0.4 M ammonia and 1.5 M hydrazine, respectively.



Figure S1. Structures of pyrene (a), 1,3,6-trinitropyrene (b), and the carbon framework of GQD-OH (c).

1.3. Photoluminescence quantum yields measurements.

The emission quantum yields of GQDs were estimated by reference to quinine sulfate ($\Phi_R = 58\%$ at 354 nm excitation) and Rhodamine 6G ($\Phi_R = 94\%$ at 490 nm excitation). The equation used for QY calculations was as follows:

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}_{\mathrm{R}} \times (I / I_{\mathrm{R}}) \times (A_{\mathrm{R}} / A) \times (\eta^2 / \eta_{\mathrm{R}}^2)$$

where Φ is the QY, *I* is the measured integrated emission intensity, η is the refractive index of the solvent, and *A* is the optical density. In order to minimize re-absorption effects, absorption in the 10 mm quartz cuvette was kept below 0.10 at the excitation wavelength. The subscript *R* refers to the reference fluorophore of the known quantum yield.

2. Characterization of GQD-OH.



Figure S2. Wide-scan XPS spectrum of the pristine GQD-OH.

Table S1. The relative atomic percentages of the 0 kGy, 50 kGy and 500 kGy irradiatedGQD-OH obtained from the deconvoluted C1s XPS peak in ambient condition.

	C-C/C=C	С-О-С/С-ОН	C=O	O-C=O
0 kGy	77	14	9	0
50 kGy	55	30	5	10
500 kGy	66	20	10	4



Figure S3. UV-Vis absorption spectrum of pristine GQD-OH.



Figure S4. PL spectra of the irradiated GQD-OH with doses from 100 to 400 kGy at different excitation wavelengths.



Figure S5. FTIR spectra of GQD-OH with the irradiation doses at 0, 50 and 500 kGy.

Table S2. Elemental Analysis of pristine, 50 and 500 kGy irradiated GQD-OH in ambient

conditions.

	C(wt%)	H(wt%)	O(wt%)
0 kGy	74.22	3.26	22.52
50 kGy	56.29	3.81	39.90
500 kGy	65.36	3.50	31.14



Figure S6. High-resolution TEM image of (a) the pristine and (b) 500 kGy irradiated GQD-OH in ambient conditions.



Figure S7. Wide-scan XPS spectra of the irradiated GQD-OH with 50 and 500 kGy doses in ambient conditions.



Figure S8. High-resolution XPS O1s spectra of irradiated GQD-OH with (a) 50 kGy and (b) 500 kGy dose in ambient conditions. The deconvolution of O1s spectra of irradiated GQD-

OH yields the following four peaks: peak I (530.4-530.6 eV) corresponding to C=O groups in carbonyl and quinone; peak II (531.8-532.2 eV) to C=O groups in carboxyl groups; peaks III (532.2-533) to hydroxyls or ethers; and peak IV (534.4-535.5) to chemisorbed oxygen and/or water.



Figure S9. Wide-scan XPS spectrum of the 50 kGy irradiated GQD-OH in the presence of ethanol.



Figure S10. UV-Vis absorption spectrum of 0-500 kGy irradiated GQD-OH.

Atomic force microscopy (AFM) was used to investigate the height of GQD-OH. According to AFM measurements, the height of GQD-OH before and after gamma irradiation didn't change obviously, which is nearly 5 nm. The GQD-OH was synthesized by a wet chemistry method, which was difficult to produce a single layer carbon cores.



Figure S11. AFM images of (a) pristine, (b) 50 kGy and (c) 500 kGy irradiated GQD-OH in ambient conditions.

3. Investigations of other GQDs.

3.1. Irradiation of GQDs-NH₂.

To further confirm the PL modulation and stability of the GQDs through irradiation with gamma-ray, several other types of GQDs containing different chemical groups were also investigated. The PL properties of irradiated GQD-NH₂ are shown in Figure S12. The optimal excitation peak of GQD-NH₂ changed from 480 to 400 nm after 500 kGy irradiation, showing similar variation trend with irradiated GQD-OH.



Figure S12. PL spectra of the irradiated GQD- NH_2 with doses from 0 to 500 kGy in ambient conditions.

3.3. Irradiation of m-GQDs.

The PL of m-GQDs exhibited similar variation trend with the irradiated GQD-OH (Figure S13). The optimal excitation peak of m-GQDs changed from 420 to 400 nm after 500 kGy irradiation.



Figure S13. PL spectra of the irradiated m-GQDs with doses from 0 to 500 kGy in ambient conditions.



Figure S14. The cellular viability of 4T1 cancer cells with different concentrations of pristine, 50 and 500 kGy irradiated GQD-OH. C₀ is the concentration of the pristine GQD-OH solution.







Figure S16. UV-Vis spectra of the irradiated GQD-OH containing ethanol with the dose of 0, 50 and 500 kGy.