Supporting Information

Gamma Ray Shifted and Enhanced Photoluminescence of Graphene Quantum Dots

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Both authors have contributed equally to this work.
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-NH$_2$, and m-GQDs.

GQD-OH, GQD-NH$_2$, and m-GQDs were synthesized by modifying a previously reported method.\textsuperscript{22} Briefly, 1,3,6-trinitropyrene (Figure S1b) was obtained through filtering the nitration production of pyrene (Figure S1a) under refluxing and stirring in HNO$_3$ 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 μm 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-NH$_2$, 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.
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:

$$\Phi = \Phi_R \times \left( \frac{I}{I_R} \right) \times \left( \frac{A_R}{A} \right) \times \left( \frac{\eta^2}{\eta_R^2} \right)$$

where $\Phi$ is the QY, $I$ is the measured integrated emission intensity, $\eta$ 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 irradiated GQD-OH obtained from the deconvoluted C1s XPS peak in ambient condition.

<table>
<thead>
<tr>
<th></th>
<th>C-(\text{C}/\text{C}=\text{C})</th>
<th>C-(\text{O}-\text{C}/\text{C}=\text{OH})</th>
<th>(\text{C}=\text{O})</th>
<th>O-(\text{C}=\text{O})</th>
</tr>
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<tbody>
<tr>
<td>0 kGy</td>
<td>77</td>
<td>14</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>50 kGy</td>
<td>55</td>
<td>30</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>500 kGy</td>
<td>66</td>
<td>20</td>
<td>10</td>
<td>4</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th></th>
<th>C(wt%)</th>
<th>H(wt%)</th>
<th>O(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kGy</td>
<td>74.22</td>
<td>3.26</td>
<td>22.52</td>
</tr>
<tr>
<td>50 kGy</td>
<td>56.29</td>
<td>3.81</td>
<td>39.90</td>
</tr>
<tr>
<td>500 kGy</td>
<td>65.36</td>
<td>3.50</td>
<td>31.14</td>
</tr>
</tbody>
</table>

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](image-url). PL spectra of the irradiated GQD-NH₂ 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 S15. Diagram of the synthesis of GQD-OH.
Figure S16. UV-Vis spectra of the irradiated GQD-OH containing ethanol with the dose of 0, 50 and 500 kGy.