Supporting Information

Reduction of graphene oxide quantum dots to enhance yield of reactive oxygen species for photodynamic therapy

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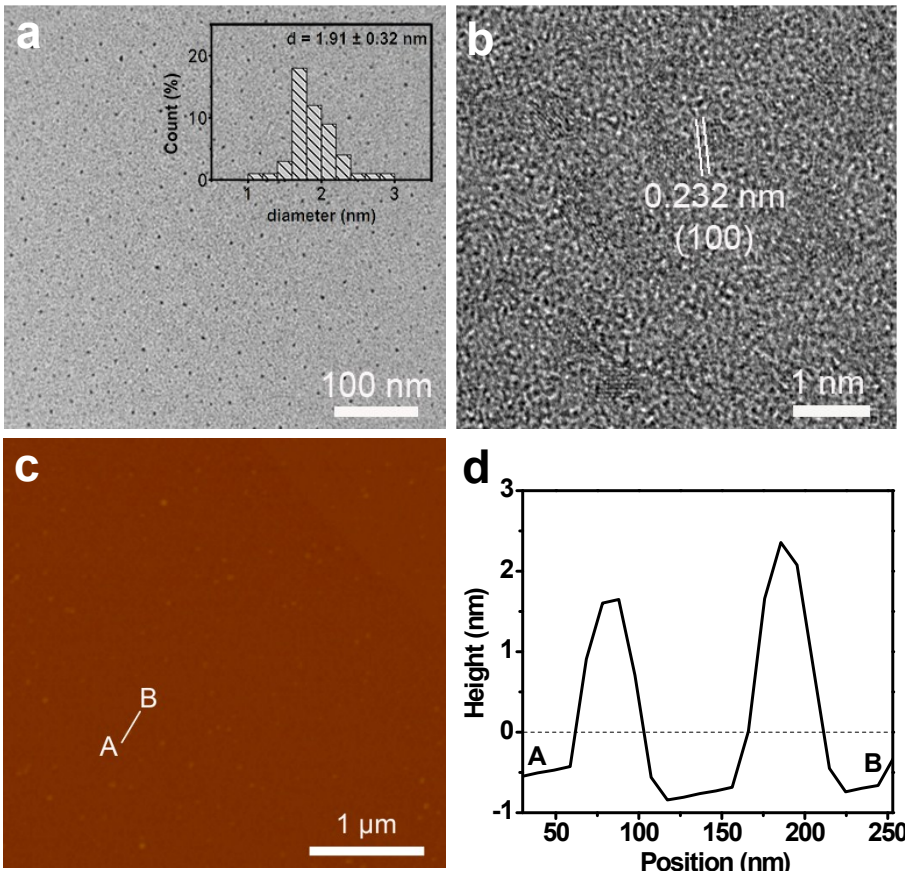

Fig. S1 (a) TEM image of GOQDs. (Inset is the size distribution of GOQDs). (b) HRTEM image of GOQDs. (c) AFM image of GOQDs and (d) their height profile analysis.

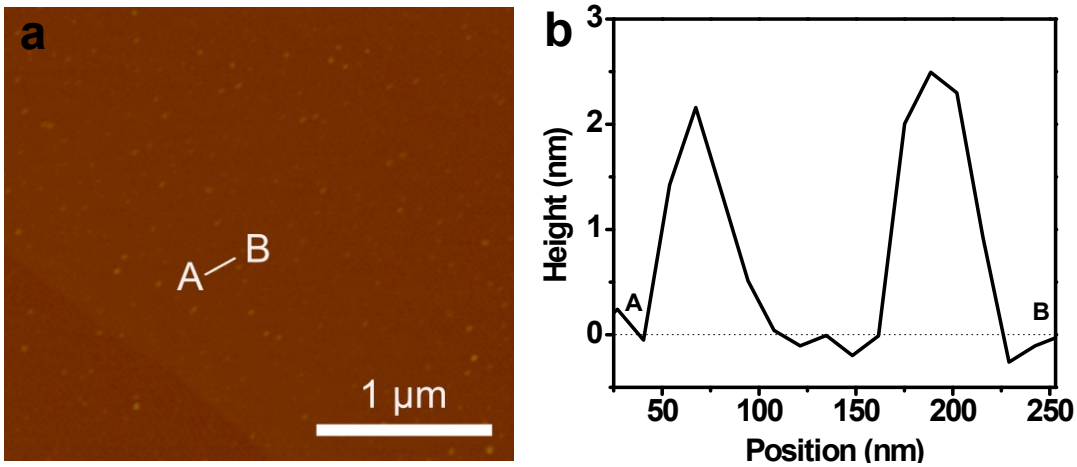

Fig. S2 (a) AFM image of rGOQDs and (b) their height profile analysis.

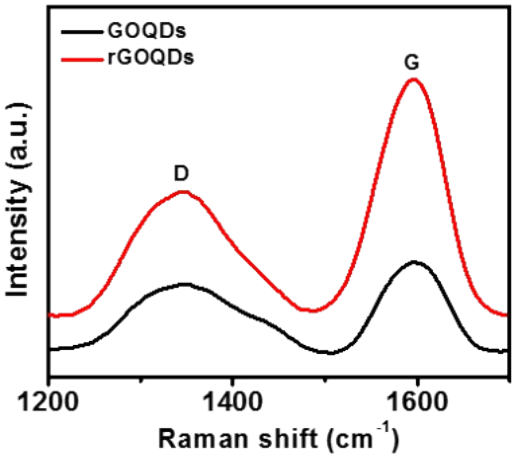

Fig. S3 Raman spectra of GOQDs (black) and rGOQDs (red).

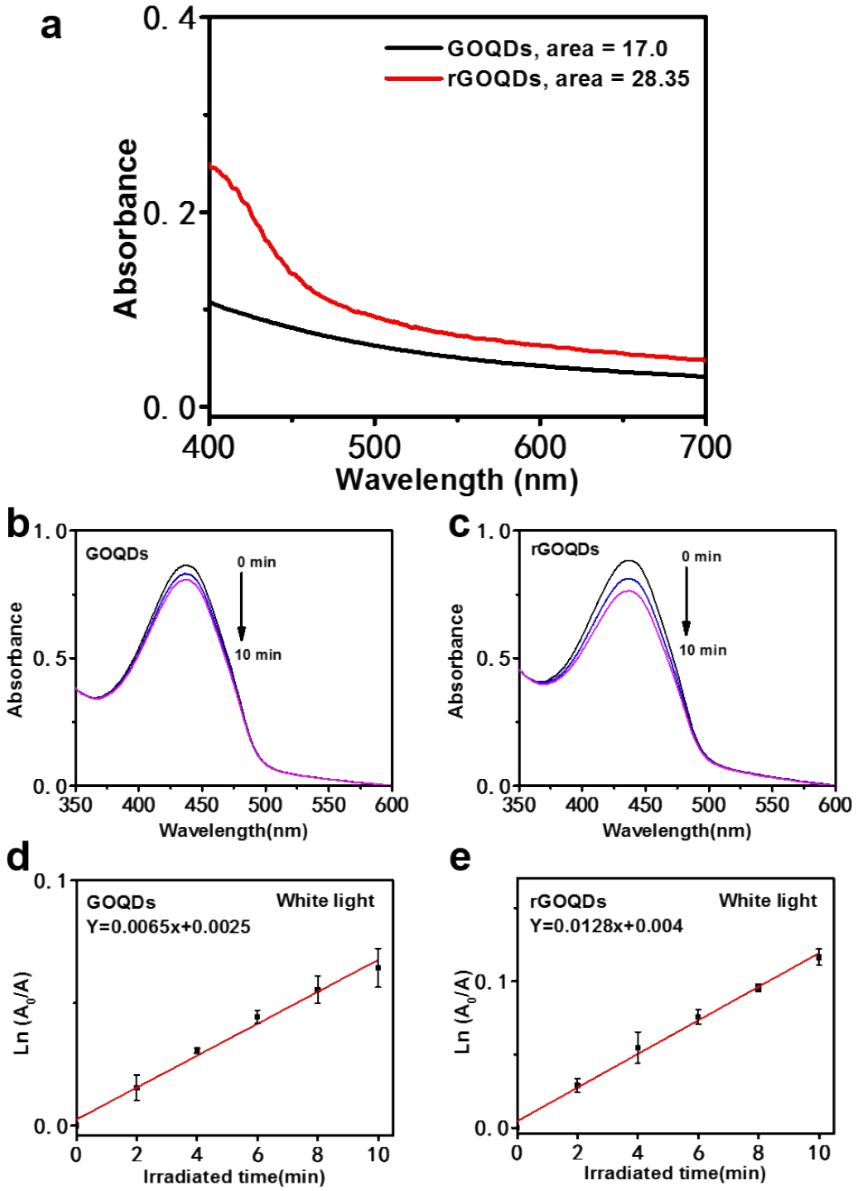

Fig. S4 The comparison of $^1O_2$ quantum yields of GOQDs and rGOQDs under white light. (a) The absorption spectra of GOQDs and rGOQDs in aqueous solution. The absorbance of RNO solution containing (b) GOQDs and (c) rGOQDs at 440 nm with the irradiation of white light for different time (0, 5, 10 min). The reducing absorbance of RNO solution containing (d) GOQDs or (e) rGOQDs at 440 nm was plotted as a function of the irradiation time of white light.

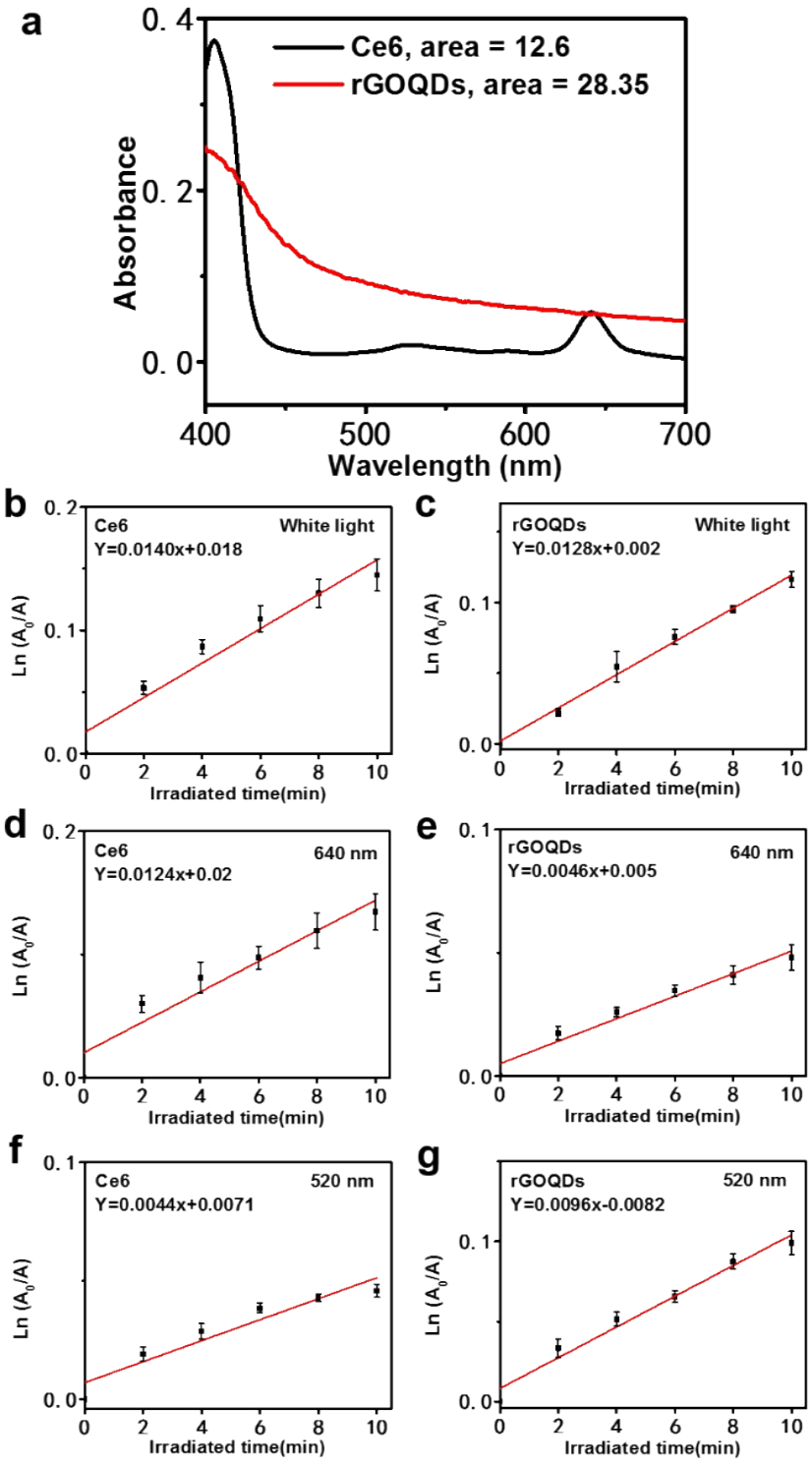

Fig. S5 The measurements of $^1O_2$ quantum yields of rGOQDs at the different excitation wavelengths. (a) The absorption spectra of rGOQDs and Ce6 in aqueous solution. The reducing absorbance of RNO solution at 440 nm in the presence of rGOQDs or Ce6 was plotted as a function of the irradiation time (b, c) with white light, (d, e) with 640 nm light, and (f, g) with 520 nm light.

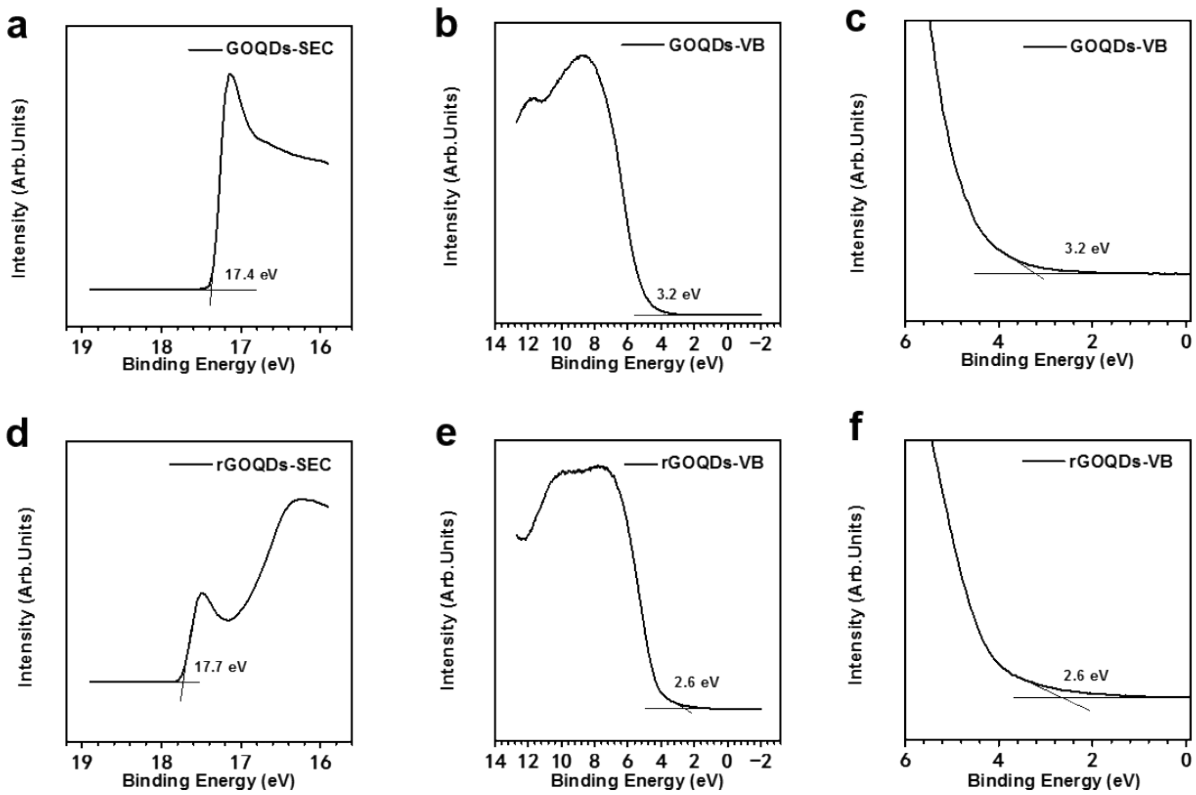

Fig. S6 Ultraviolet photoelectron spectroscopy (UPS) characterization of GOQDs and rGOQDs. (a) Secondary electron cutoff and (b) valence band of GOQDs. (c) The magnified curve of (b) at the range from 6 to 0 eV. (d) Secondary electron cutoff and (e) valence band of rGOQDs. (f) The magnified curve of (e) at the range from 6 to 0 eV. The horizontal solid lines mark the baseline and the sloping solid lines indicate the tangents of the curve. The secondary electron cutoff and valence band energy can be calculated from the intersections of the tangents with the baseline.

Table. S1 Calculation of fluorescent quantum yield (PLQY) of GOQDs and rGOQDs using 9,10-Bis (phenylethynyl) anthracene in cyclohexane as a reference.

Sample	**Integrated emission intensity (*I*)**	**Absorbance at 450 nm (*A*)**	**Refractive index of solvent (*η*)**	**PLQY (*φ*)**
9,10-Bis (phenylethynyl) anthracene	19269.3	0.065	1.4264	1
GOQDs	434.4	0.059	1.33	0.021
rGOQDs	551.1	0.069	1.33	0.024

The fluorescent quantum yield of sample was calculated according to the following equation:[1, 2]

$$\varphi_x = \varphi_{st} (I_x/I_{st}) (\eta_x^2/\eta_{st}^2) (A_{st}/A_x)$$

Where φ is the PLQY, I is the integrated fluorescence emission intensity, η is the refractive index of the solvent, and A is the optical density. The subscript "st" refers to standard with known quantum yield and "x" refers to the sample. In order to minimize re-absorption effects, absorbance in the 10 mm fluorescent cuvette was kept below 0.10 at the excitation wavelength of 450 nm.

Table. S2 The comparison of $^1O_2$ quantum yields of GOQDs and rGOQDs under white light.

λ_{ex}	A_{GOQDs}/A_{rGOQDs}	K_{rGOQDs}	K_{GOQDs}	Φ_{rGOQDs}
White light	0.600	0.0128	0.0065	$1.2\Phi_{GOQDs}$

To eliminate the inner-filter effect, the maximum absorption of samples were kept below 0.4. Imidazole and RNO were used as the $^1O_2$-trapping agent, and the absorbance of RNO at 440 nm was recorded at various irradiation times to obtain the decay rate of the photosensitizing process. The $^1O_2$ quantum yield of the rGOQDs (Φ_{rGOQDs}) in water was calculated using the following formula[3]:

$$\Phi_{rGOQDs} = \Phi_{GOQDs} * K_{rGOQDs} * A_{GOQDs} / (K_{GOQDs} * A_{rGOQDs})$$

where K_{rGOQDs} and K_{GOQDs} are the decay rate of absorption of RNO solution at 440 nm caused by rGOQDs and GOQDs, respectively. A_{rGOQDs} and A_{GOQDs} represent the absorbance of rGOQDs and GOQDs, respectively, which are determined by integration of the optical absorption spectrum in the wavelength range of 400–700 nm. Φ is $^1O_2$ quantum yield.

Table. S3 The measurements of $^1O_2$ quantum yields of rGOQDs at the different excitation wavelengths.

λ_{ex}	A_{Ce6}/A_{rGOQDs}	K_{rGOQDs}	K_{Ce6}	Φ_{rGOQDs}
White light	0.445	0.0128	0.0140	$0.40\Phi_{Ce6}$
640 nm	1.027	0.0046	0.0124	$0.38\Phi_{Ce6}$
520 nm	0.197	0.0096	0.0044	$0.43\Phi_{Ce6}$

$^1O_2$ quantum yield was measured via the chemical method by using imidazole and RNO as the $^1O_2$-trapping agent,[4] and Ce6 as the standard photosensitizer.[5] To eliminate the inner-filter effect, the maximum absorbance of Ce6 and rGOQDs was kept below 0.4. The absorbance of RNO at 440 nm was recorded at various irradiation times to obtain the decay rate of the photosensitizing process. The $^1O_2$ quantum yield of rGOQDs (Φ_{rGOQDs}) in water was calculated by using the following formula[3]:

$$\Phi_{rGOQDs} = \Phi_{Ce6} * K_{rGOQDs} * A_{Ce6} / (K_{Ce6} * A_{rGOQDs})$$

where K_{rGOQDs} and K_{Ce6} are the reducing absorbance of RNO at 440 nm caused by rGOQDs and Ce6, respectively. A_{rGOQDs} and A_{Ce6} represent the absorbance of GOQDs and Ce6, respectively, which are determined by integration of the optical absorption spectrum in the wavelength range of 400–700 nm. Φ_{Ce6} is $^1O_2$ quantum yield of Ce6.

References

1 S. Zhu, J. Zhang, C. Qiao, S. Tang, Y. Li, W. Yuan, B. Li, L. Tian, F. Liu, R. Hu, H. Gao, H. Wei, H. Zhang, H. Sun and B. Yang, *Chem. Commun.*, 2011, **47**, 6858-6860.

2 I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin, D. Y. Vorobyev, N. M. Bazhin and E. Vauthey, *J. Photoch. Photobio. A*, 2006, **181**, 37-43.

3 M. Hoebeke and X. Damoiseau, *Photochem. Photobiol. Sci.*, 2002, **1**, 283–287.

4 B. Tian, C. Wang, S. Zhang, L. Feng and Z. Liu, *ACS Nano*, 2011, **5**, 7000-7005.

5 R. K. Pandey, D. A. Bellnier, K. M. Smith and T. J. Dougherty, *Photochem. Photobiol.*, 1991, **53**, 65-72.