Supporting Information *for*

Fluorine-containing graphene quantum dots with a high singlet oxygen generation applied for photodynamic therapy

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Fig. S1 a) A typical TEM image (inset: HRTEM image) and b) Particle size distribution of the GQDs sample.



Fig. S2 a) Raman spectrum of the GQDs sample. b) XPS survey spectrum of the GQDs sample, c) High resolution C1s spectra (black and red) of the GQDs sample and d) High resolution N1s spectra (black and red) of the GQDs. Solid-black lines are experimental whereas solid-red lines are the best curve fitting.



Fig. S3 FT-IR spectra of F-GQDs and GQDs.



Fig. S4 a) PL emission spectra of the GQDs sample $(200 \ \mu g \ mL^{-1})$ dispersed in aqueous solution (inset: photographs of the GQDs sample under visible daylight (Vis) and an UV lamp at 365 nm (UV)). b) Fluorescence decay curve of the GQDs sample.



Fig. S5 a) PL intensities of F-GQDs and GQDs aqueous solutions changing with different pH values. b) PL intensities of F-GQDs and GQDs aqueous solutions at different temperatures. c) PL intensities of F-GQDs and GQDs in the PBS at different temperatures.



Fig. S6 a) ESR spectra of TEMP + F-GQDs (200 μ g mL⁻¹) in the dark or under light irradiation for 12 min. b) ESR spectra of TEMP + F-GQDs under different light irradiation time.



Fig. S7 a) ESR spectra of TEMP + GQDs (200 μ g mL⁻¹) in the dark or under light irradiation for 12 min. b) ESR spectra of TEMP + GQDs under different light irradiation times. c) ESR spectra of TEMP + H₂O under different light irradiation times.



Fig. S8 Images of HepG2 3D MCs captured by optical microscope in 7 days. Scale bars $= 100 \ \mu m$.



Fig. S9 a) MTT results (24 h) for HepG2 cells co-incubated with increasing concentration of the GQDs sample. b) The fluorescence intensity of the HepG2 cells co-incubated with 200 μ g mL⁻¹ of F-GQDs with (yellow) and GQDs (blue) for 6 h, as quantified by a flow cytometry. The mean fluorescence unit (MFU) was the average of 10,000 cells. CLSM images of c) the HepG2 cells. (scale bars = 10 μ m) and (d) 3D MCs co-incubated with the GQDs sample (200 μ g mL⁻¹) for 6 h under bright-field (left panel) and under 405 nm wavelength excitation (right panel, scale bars = 50 μ m).



Fig. S10 MTT results for the HepG2 cells co-incubated with 200 μ g mL⁻¹ of the GQDs sample a) in the dark or under LED light irradiation for 12 min, respectively. b) Typical images of the HepG2 3D MCs co-incubated with DMEM and 200 μ g mL⁻¹ of the GQDs sample respectively, recorded via optical microscopy up to 7 days. The optical microscopy images were captured in the dark or under LED light irradiation (12 min) every day. Scale bars = 50 μ m.



Fig. S11 Variation of 3D MCs diameters when co-cultivated with a) DMEM(control),b) F-GQDs and c) GQDs in dark or light environment, respectively.



Fig. S12 CLSM images of the HepG2 cells stained with Calcein-AM (green) and PI (red) after co-incubated with 200 μ g mL⁻¹ of the GQDs sample for 6 h. These images were captured in the dark or under LED light irradiation (12 min). Scale bars = 50 μ m.



Fig. S13 The fluorescence intensity of HepG2 cells by a flow cytometry stained with Calcein-AM and PI after co-incubated with DMEM (a) in darkness and (d) under LED light irradiation for 12 min; 200 μ g mL⁻¹ of GQDs (b) in darkness and (e) under LED light irradiation for 12 min; 200 μ g mL⁻¹ F-GQDs (c) in darkness and (f) under LED

light irradiation for 12 min.



Fig. S14 Fluorescence intensities detected using a flow cytometer of HepG2 cells stained with DCFH-DA after co-incubated respectively with DMEM, 200 μ g mL⁻¹ F-GQDs sample and 200 μ g mL⁻¹ GQDs sample under LED light irradiation for 12 min.

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Sample	Carbon [at.%]	Oxygen [at. %]	Fluorine [at. %]
Fluorinated Graphite	49.14	0.71	50.15
F-GO	84.38	7.86	7.76
F-GQDs	63.05	29.57	1.43
GQDs	54.43	40.14	-

Table S1. XPS elemental analysis of Fluorinated Graphite, F-GO, F-GQDs and GQDs.

Heteroatom-doped GQDs	QY(%)	References
N-GQDs	24.8	48
N-GQDs	7.4	49
N-GQDs	43	50
GQDs-F	7.5	35
GQDs-P	7.3	35
S-GQDs	0.79	43
S,N-GQDs	41	51
N, F and S co-doped GQDs	70	31

Table S2. Comparison of fluorescence QYs of various heteroatom-doped GQDs.