Novel Sustainable Carbon Dot as Dual Replacements for Emulsion Stabilizers and Photoinitiators in Macroporous Polymerized High Internal Phase Emulsion Fabrication

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Keywords: carbon dots; emulsion stabilizer; photoinitiator; macroporous PolyHIPEs; enlarged pore throats; fluid permeability; cell permeability

Complementary Results

PolyHIPEs emulsion stability time and polymerization rate

Table S1. Material composition of various PolyHIPEs (20 vol% organic phase, 80 vol% water phase)

	Orangic phase			Carbon dots	Conventional emulsion stabilizer/photoinitiator	
	EHA (wt%)	IBOA (wt%)	TMPTA (wt%)	GW CDs (wt% ratio in Organic phase)	Hypermer B246 (wt% ratio in Organic phase)	TPO (wt% ratio in Organic phase)
1% GW CDs-PolyHIPE	42	42	16	1	-	-
2% GW CDs-PolyHIPE	42	42	16	2	-	-
4% GW CDs-PolyHIPE	42	42	16	4	-	-
6% GW CDs-PolyHIPE	42	42	16	6	-	-
8% GW CDs-PolyHIPE	42	42	16	8	-	-
10% GW CDs-PolyHIPE	42	42	16	10	-	-
12% GW CDs-PolyHIPE	42	42	16	12	-	-
14% GW CDs-PolyHIPE	42	42	16	14	-	-
4% Hypermer/TPO-PolyHIPE	42	42	16	-	4	4

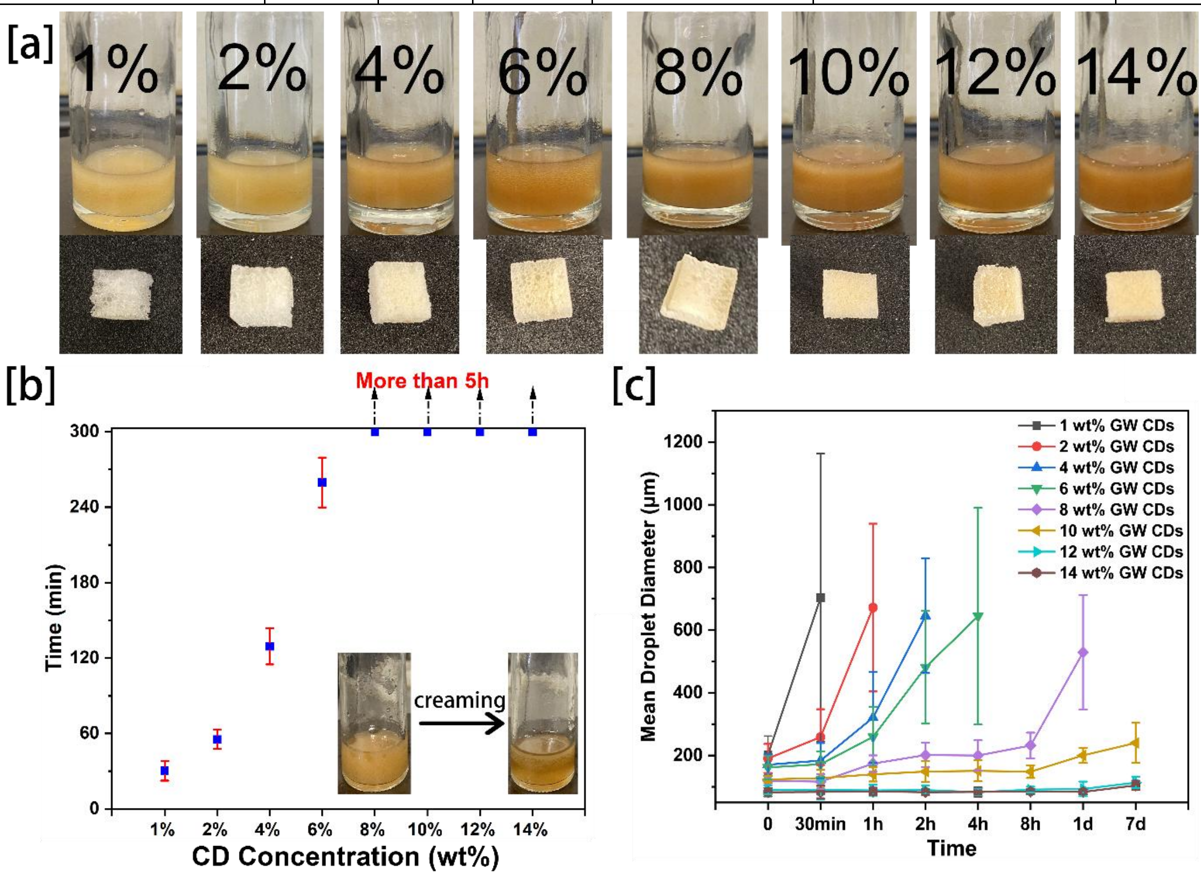

Figure S1. (a) Stable emulsions containing different GW CDs mass ratios and their cured PolyHIPEs. (b) The stability time of each emulsion. (c) Long-term emulsion stability of emulsions stabilized with varying concentrations of GW CDs.

Thermogravimetric Analysis (TGA) of GW CDs

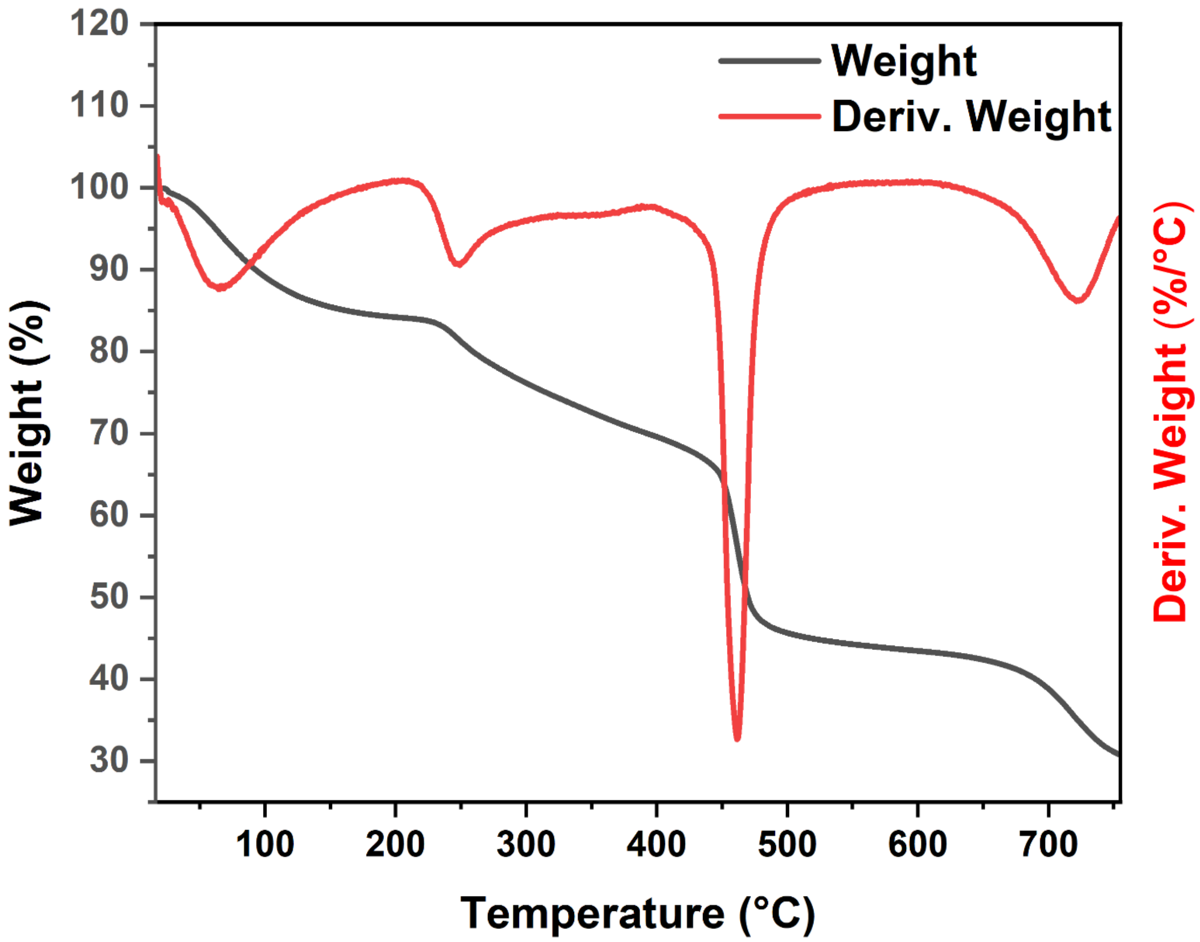

Figure S2.TGA spectrum of GW CDs.

O1s XPS spectrum and detailed XPS spectra of GW CDs

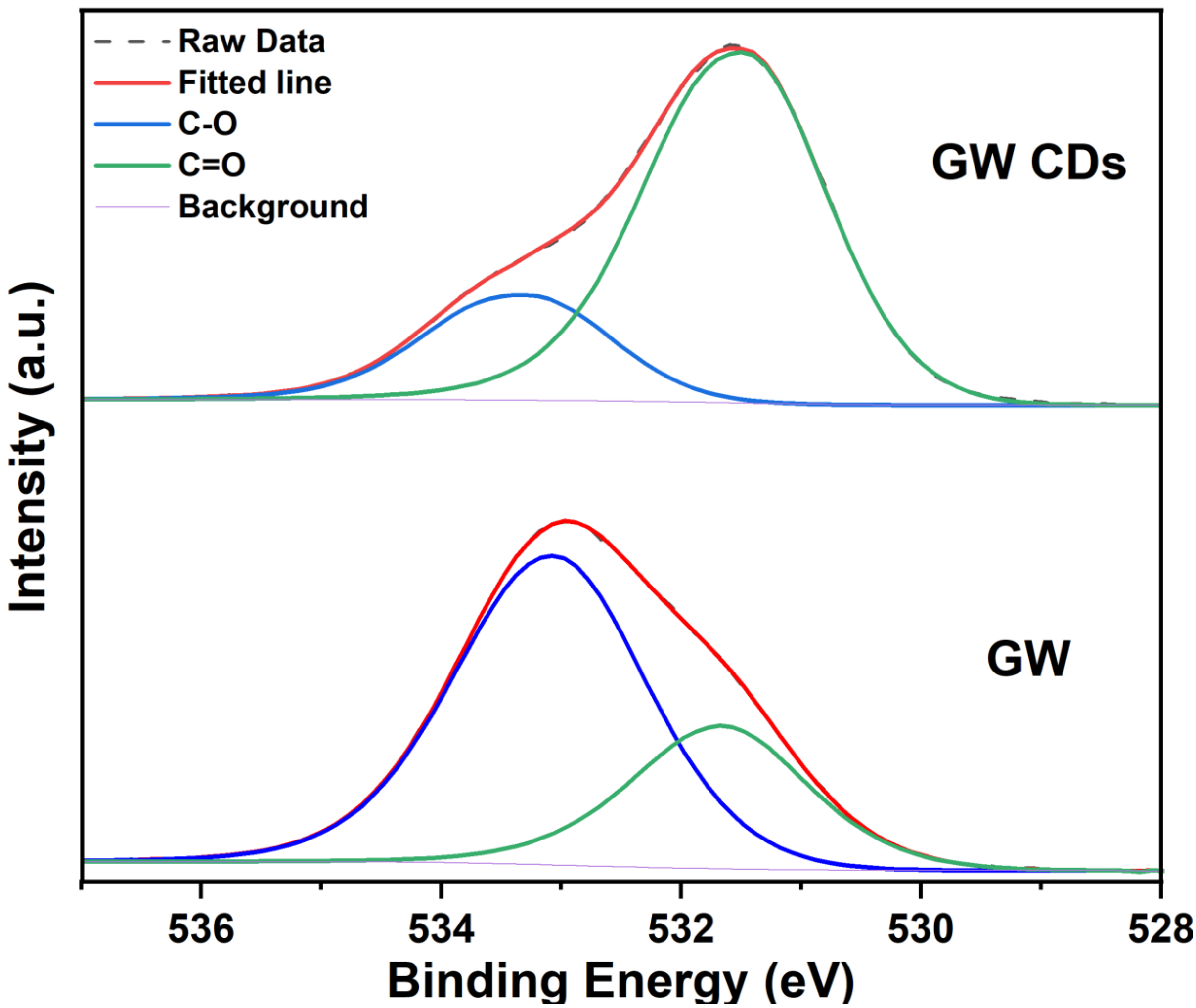

Figure S3. O1s XPS spectra of GW and GW CDs.

Table S2. The contents of each element and group in GW CDs obtained by full XPS spectrum and high-resolution C1s and O1s XPS spectra.

		GW CDs（%）	Gromwell root waste（%）
Full Spectrum	O	29.13	27.45
	N	1.18	1.98
	Ca	3.73	3.73
	K	0.85	0.19
	C	63.58	66.99
	Si	-	1.47
	Al	-	0.68
C1s	sp^3 C/ sp^2 C	38.49	48.06
	C-O	29.92	18.87
	C-N	6.42	20.01
	C=O/O-C=O	22.64	12.55
	π-π* satellite	2.53	0.5

O1s	C-O	38.22	69.71
	C=O	61.78	30.29

HLB test of GW CDs

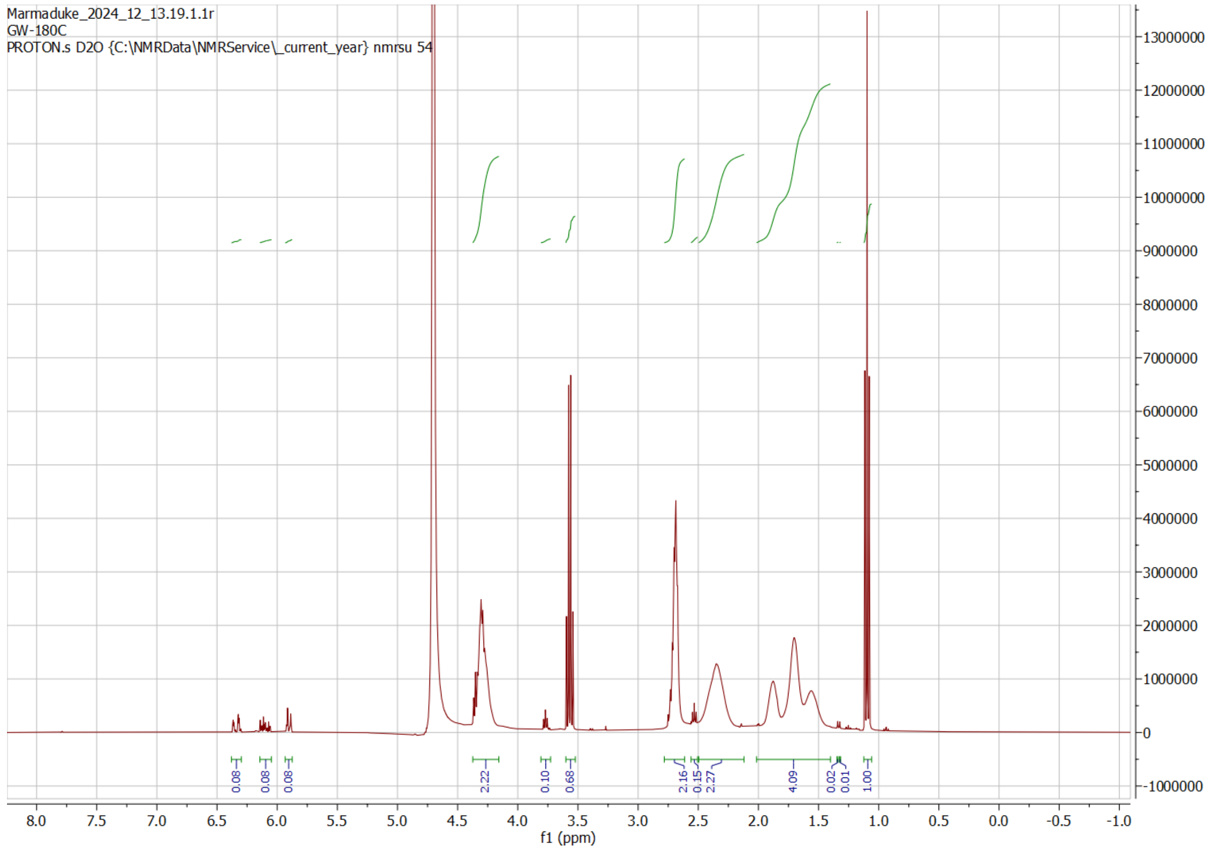

Figure S4. **^{1}H NMR spectrum of GW CDs and the integration of each peak, with the peak at 1-1.15ppm as the reference peak (area = 1)**

Table S3. Integration of hydrophilic and hydrophobic peaks in ^{1}H NMR and calculated HLB of GW CDs

Hydrophobic groups		**Hydrophilic groups**	
Signal (ppm)	Integration	Signal (ppm)	Integration
<1	0.03	3.2-3.3	0.01
1-1.15	1	2.6-2.8	2.22
1.15-1.3	0.11	3.5-3.6	0.65
1.3-1.4	0.06	3.72-3.8	0.1
1.4-2.1	4.12	4.15-4.4	2.31
2.1-2.5	2.28		
2.5-2.56	0.19		
5.87-6.38	0.26		
Total	8.05	Total	5.29
According to the formula 2, HLB= 7.39			

PLQY test of GW CDs

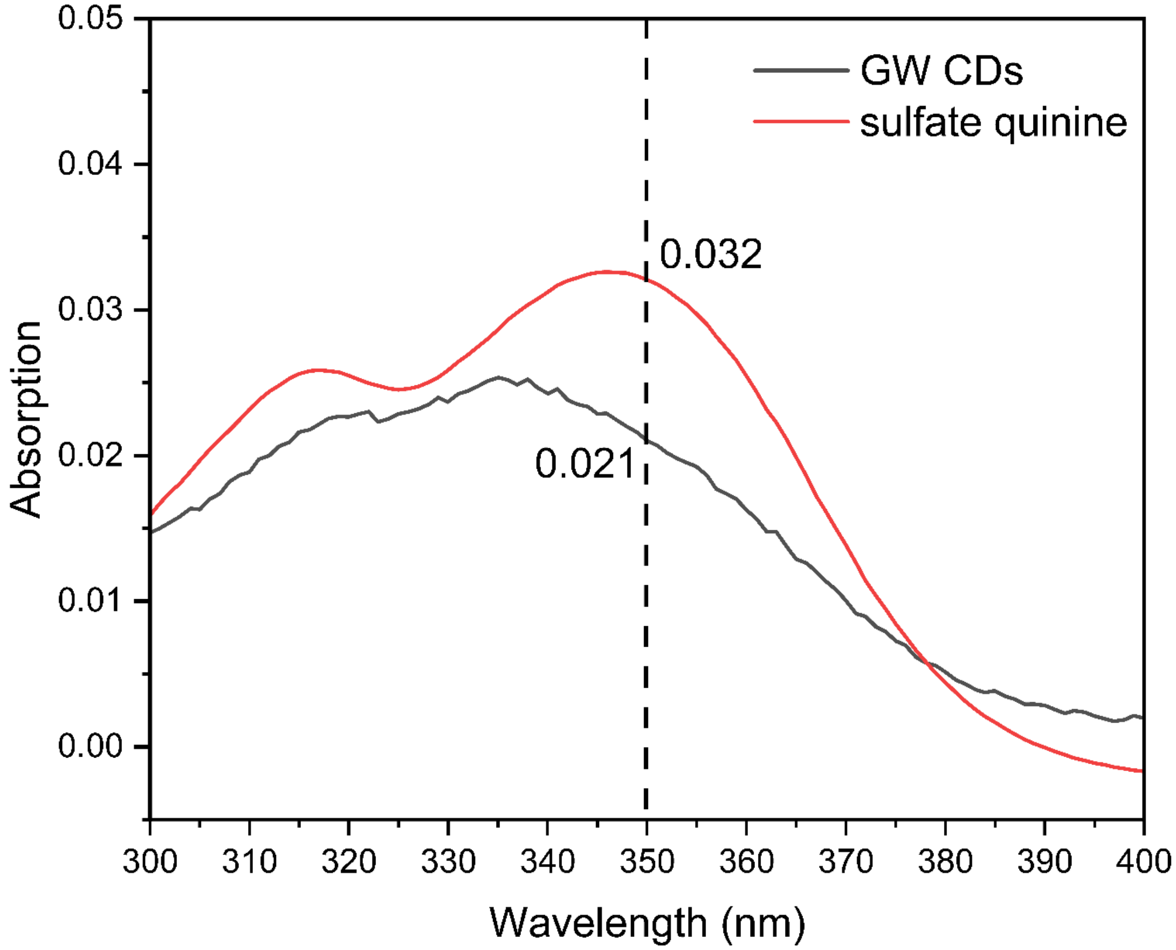

Figure S5. Comparison of the absorbance of quinine sulfate solution and GW CDs solution under 350nm UV light. The absorbance less than 0.1 can be regarded as the same refractive index.

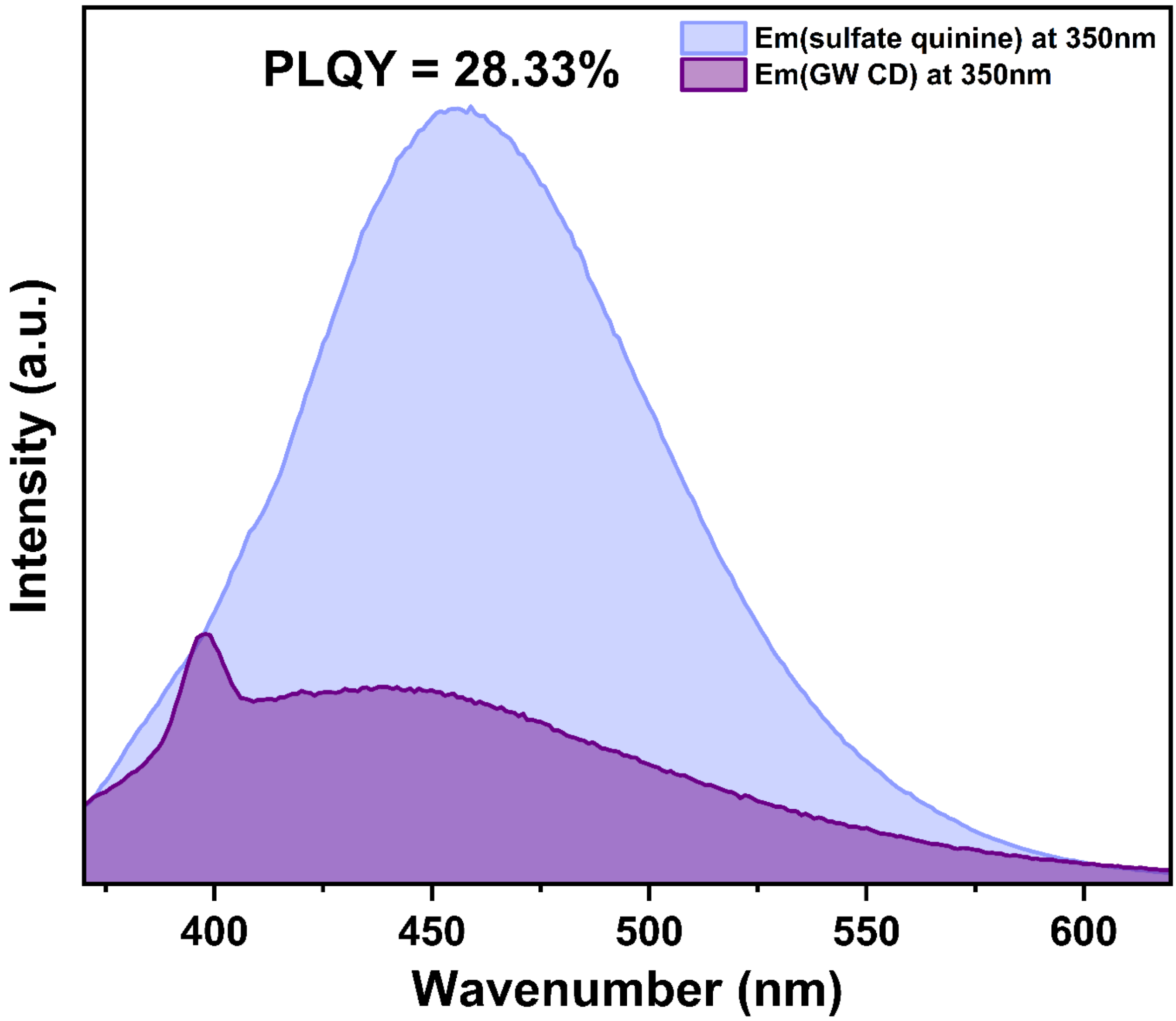

Figure S6. Comparison of the fluorescence emission intensities of quinine sulfate solution and GW CDs solution under 350nm UV light. The absorbance less than 0.1 can be regarded as the same refractive index. According to the formula 3 and figure S5, $\frac{A_{QS}}{A_{GW\ CDs}}$ = 1.524, $\frac{S_{GW\ CDs}}{S_{QS}}$ = 0.344, $PLQY_{GW\ CDs}$=28.33%

XRD of GW CDs before and after UV Exposure

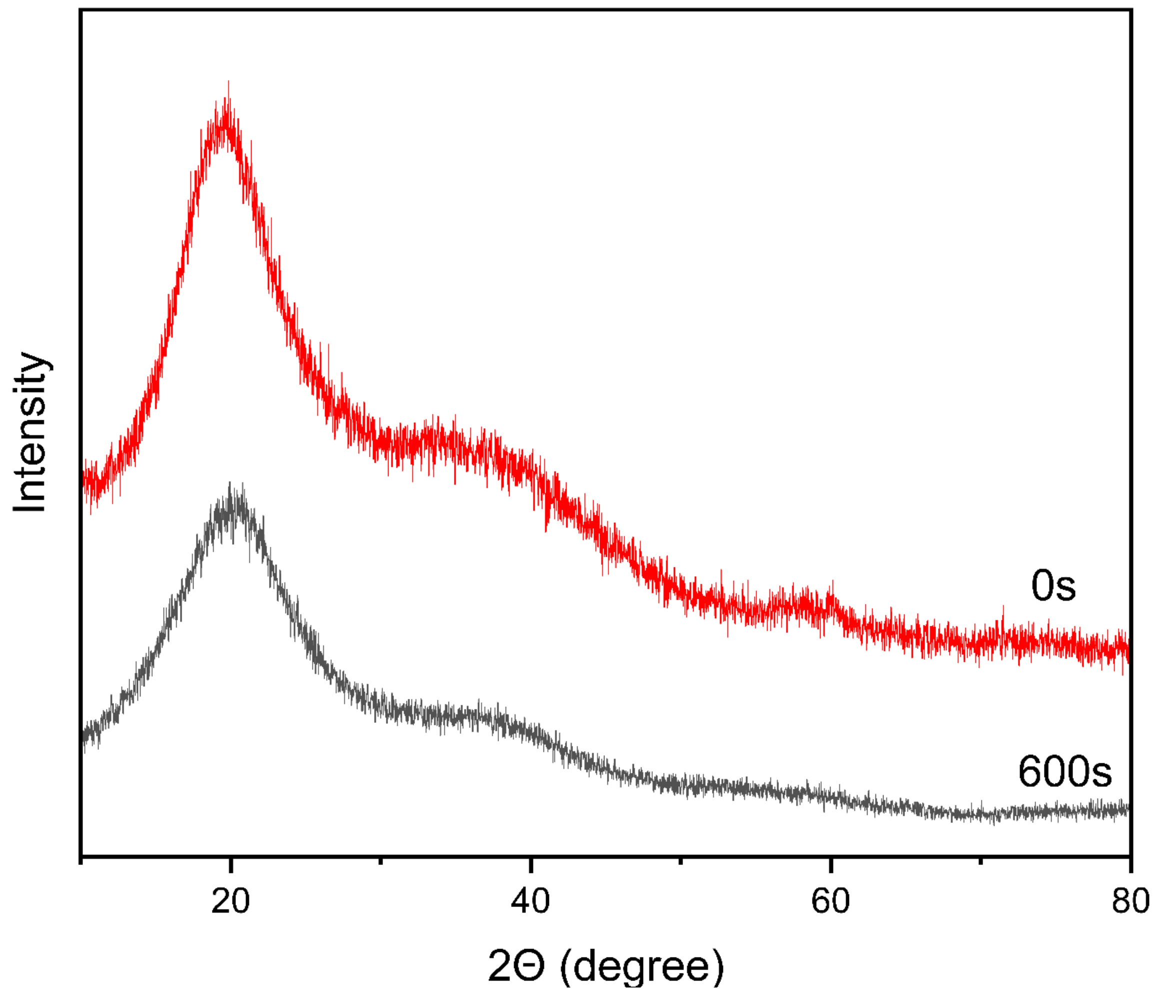

Figure S7. XRD of GW CDs before and after UV irradiation.

TEM Pictures of GW CDs after UV Exposure

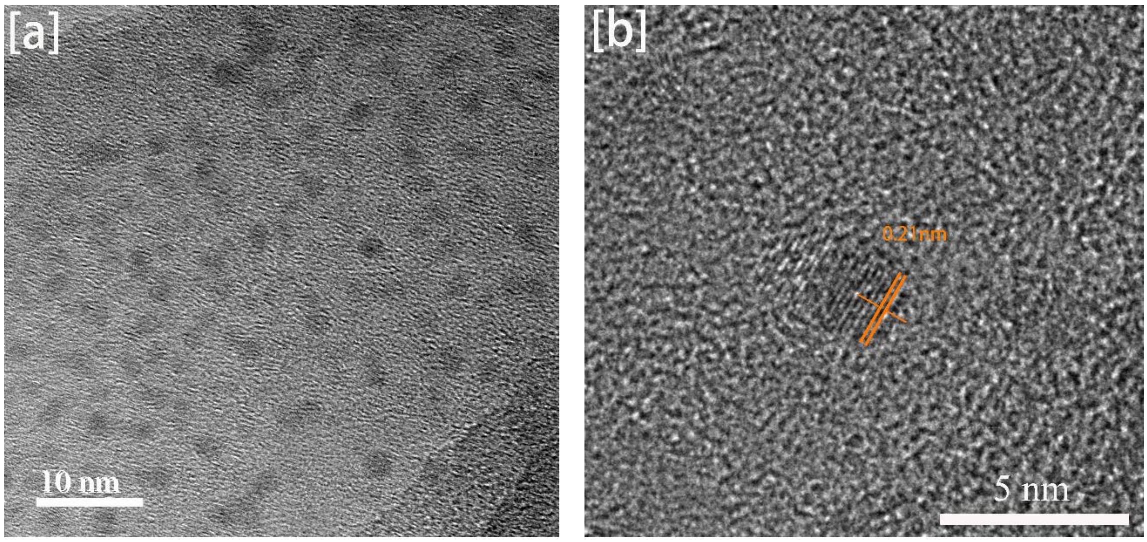

Figure S8. TEM image (a) of GW CDs after UV irradiation for 600s and high-resolution TEM image (b) of GW CDs.

Simulated EPR spectra, EPR spectrum of GW CDs aqueous solution after oxygen removal and EPR spectra of prepolymer/GW CDs ethanol solution

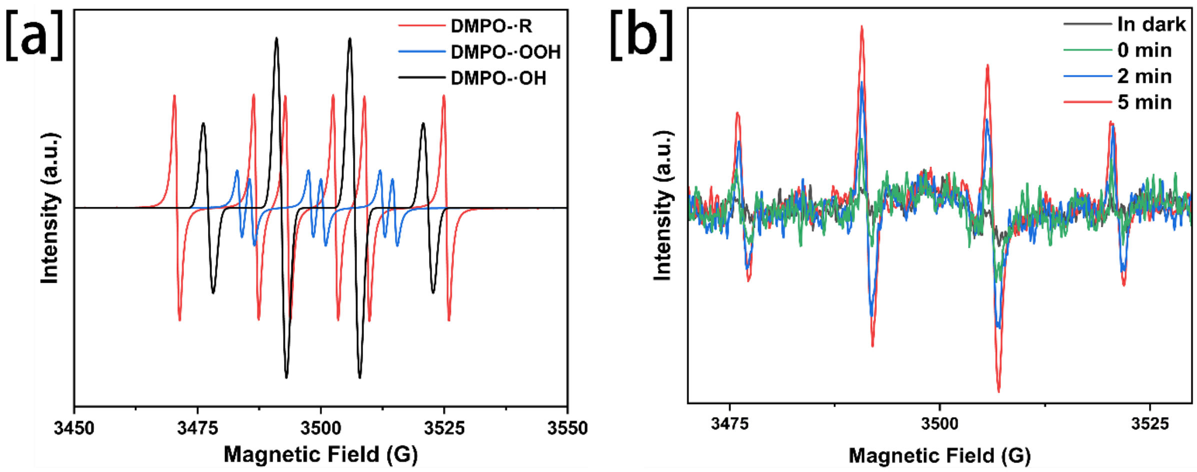

Figure S9. (a): Simulated EPR spectra trapped by the DMPO provided by the program Easyspin. Simulations resulted in DMPO-•OH: g = 2.00592, A_N = 14.9 G, and A_H = 14.9 G. DMPO-•R: g = 2.00592, A_N = 16.0 G, and A_H = 23.3 G. DMPO-•OOH: g = 2.00592, A_N = 12.0 G, and A_H = 2.5 G. (b): EPR spectra of radicals trapped by DMPO in deoxygenated water under 365 nm UV irradiation for varying durations, cGW CDs=10 mg/mL, cDMPO = 4 mg/mL.

The morphology comparation of cells in media containing GW CDs and Hypermer B246/TPO

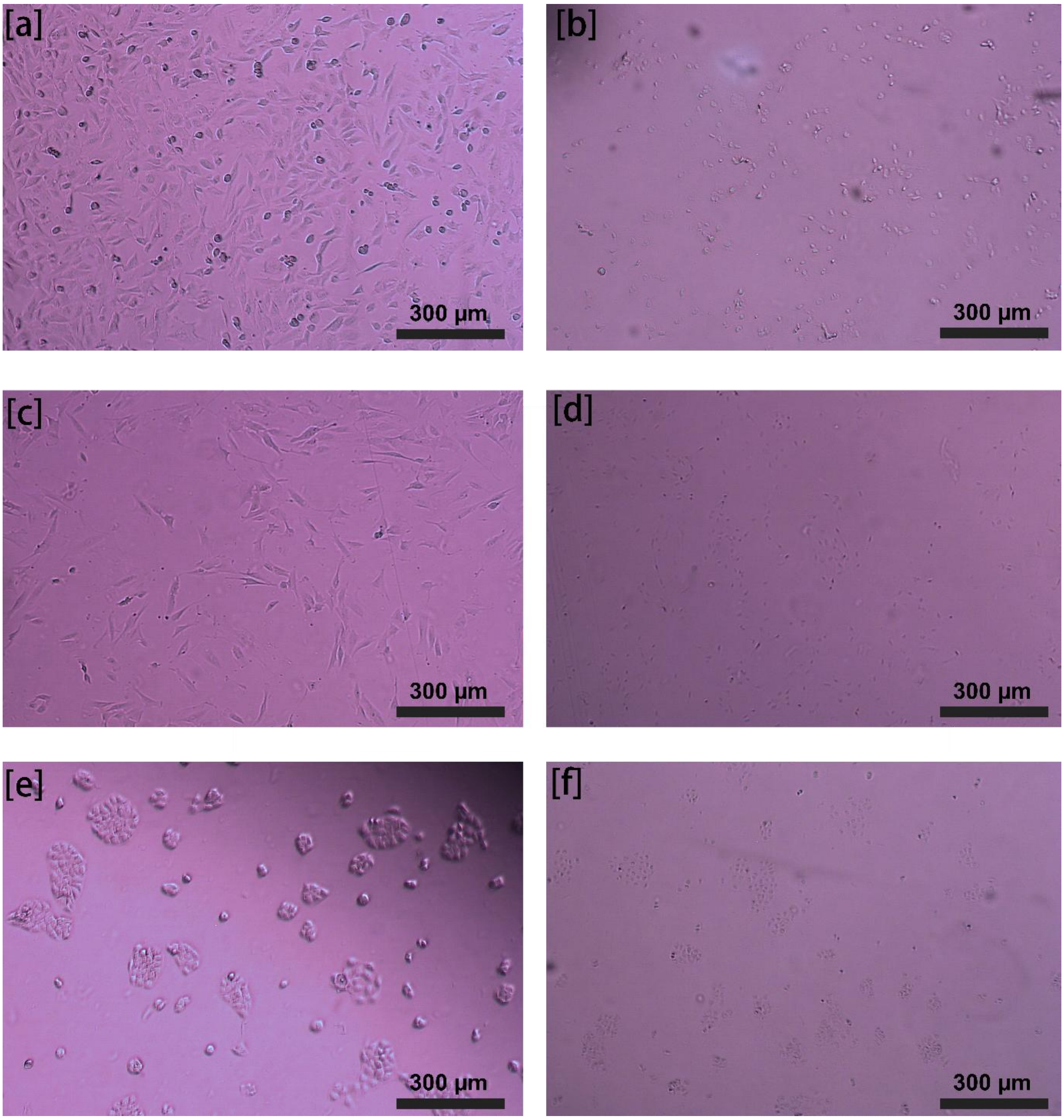

Figure S10. The morphology of BJ5TA cells in media containing GW CDs (a) and Hypermer B246/TPO (b) with 10× magnification. The morphology of MLO-A5 cells in media containing GW CDs (c) and Hypermer B246/TPO (d) with 10× magnification. The morphology of HaCaT cells in media containing GW CDs (e) and Hypermer B246/TPO (f) with 10× magnification. All the scale bar is 300 µm.

The EEM of GW CDs without Rayleigh and Raman scattering removed

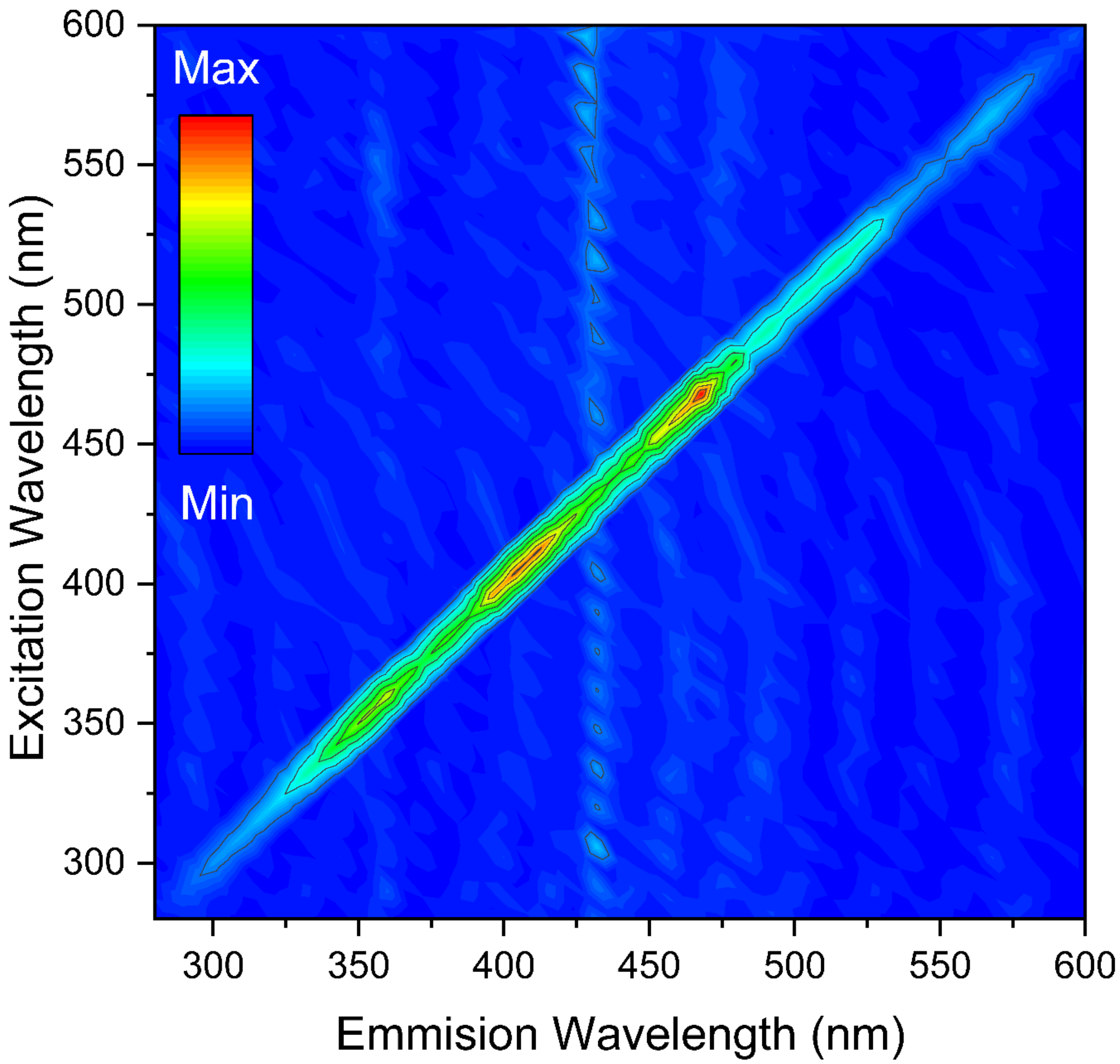

Figure S11. EEM of GW CDs without Rayleigh and Raman scattering removed

The average pore size, the average number of pore throats per pore, and the average pore throat diameter for each PolyHIPE sample.

Table S4. The average pore diameter, the average number of pore throats per pore, and the average pore throat diameter of each PolyHIPE sample.

	The average pore size (μm)	The average number of pore throats per pore	The average pore throat diameter (μm)
1% GW CDs-PolyHIPE	834±498	4.3±1.7	121±62

2% GW CDs-PolyHIPE	588±363	2.8±1.5	105±73
4% GW CDs-PolyHIPE	363±161	4.7±1.7	89±52
6% GW CDs-PolyHIPE	310±111	2.6±1.5	64±33
8% GW CDs-PolyHIPE	231±86	2.8±1.3	62±42
10% GW CDs-PolyHIPE	186±63	1.5±1.3	56±25
12% GW CDs-PolyHIPE	167±40	1±0.7	31±10
14% GW CDs-PolyHIPE	144±24	0.1±0.0	35±19
4% Hypermer/TPO-PolyHIPE	51±8	16.1±8.0	3±2

The average droplets diameter of each GW CDs-stabilized emulsion at different temperatures.

Table S5. The average droplets diameter of each GW CDs-stabilized emulsion at 20, 45 and 70 °C.

	The average droplets size (μm) at 20 °C	The average droplets size (μm) at 45 °C	The average droplets size (μm) at 70 °C
1% GW CDs-PolyHIPE	258±63	537±117	901±189
2% GW CDs-PolyHIPE	218±45	428±88	633±122
4% GW CDs-PolyHIPE	174±23	258±44	383±53
6% GW CDs-PolyHIPE	129±20	211±29	322±37
8% GW CDs-PolyHIPE	103±12	160±22	245±29
10% GW CDs-PolyHIPE	93±15	137±14	203±21
12% GW CDs-PolyHIPE	89±7	120±9	171±13
14% GW CDs-PolyHIPE	86±5	104±6	121±11

The SEM image of 2%, 6%, 8% Hypermer/TPO-PolyHIPE

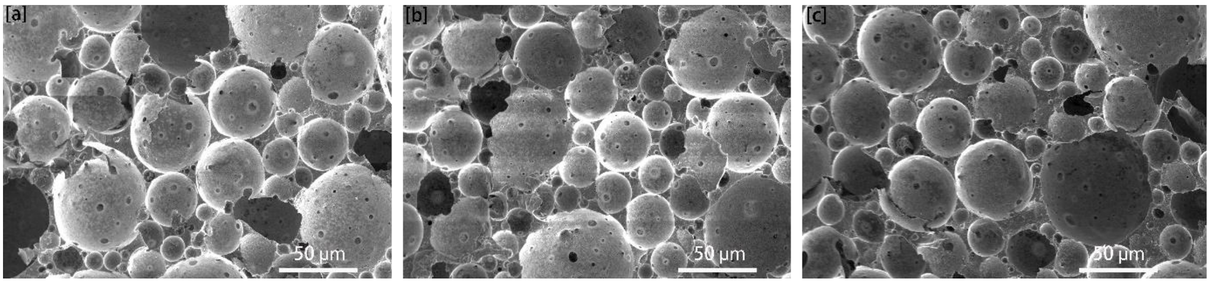

Figure S12. SEM images of PolyHIPE samples containing 2 wt% (a), 6 wt% (b), 8 wt% (c) Hypermer B246 and TPO. All the scale bar is 50 μm.

The surface temperature of the PolyHIPEs after curing

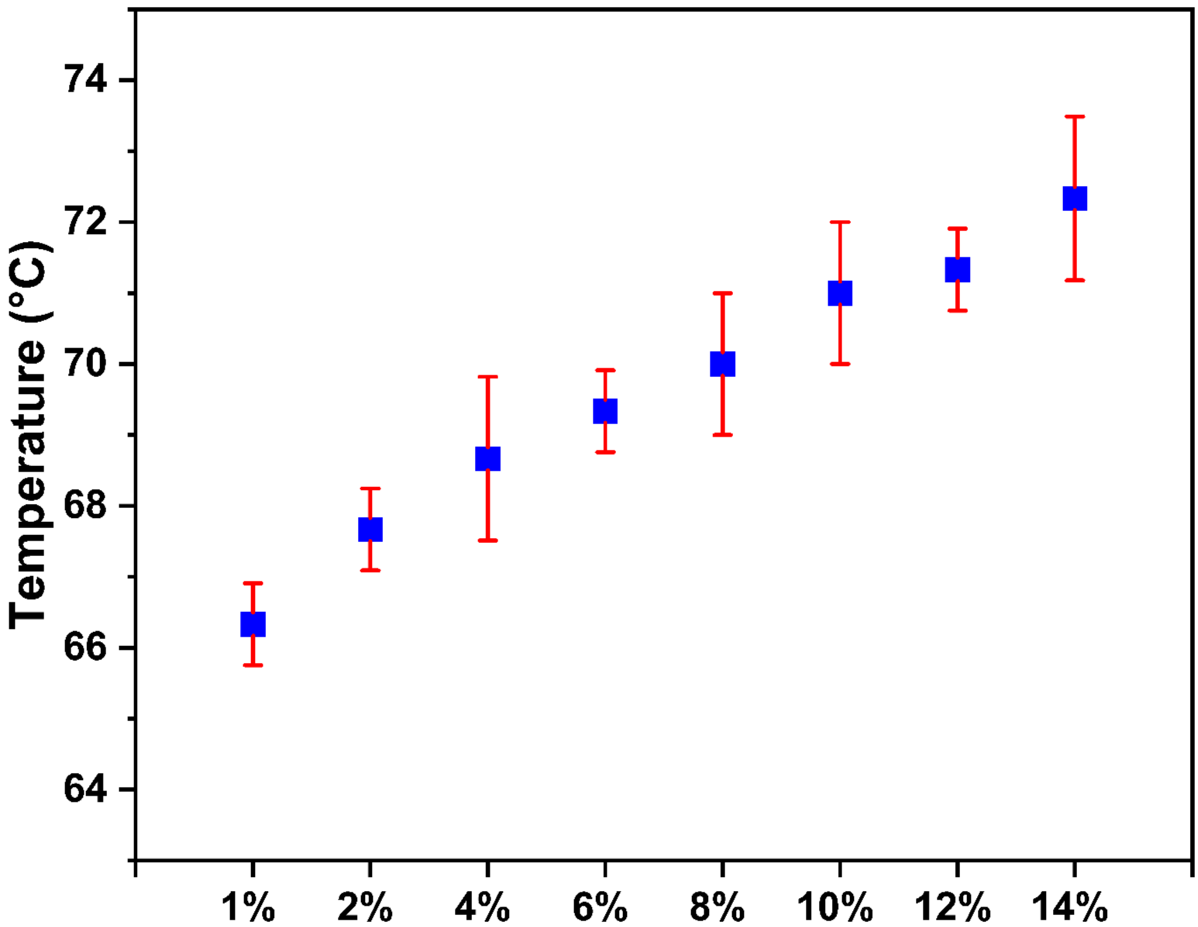

Figure S13. The surface temperature of each GW CDs-stabilized PolyHIPEs after 180 seconds of curing under 365 nm UV light at an intensity of 1700 mW/cm^2. PolyHIPE samples containing 1 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, 12% wt% and 14 wt% GW CD were abbreviated into 1%, 2%, 4%, 6%, 8%, 10%, 12%, 14% in figures.

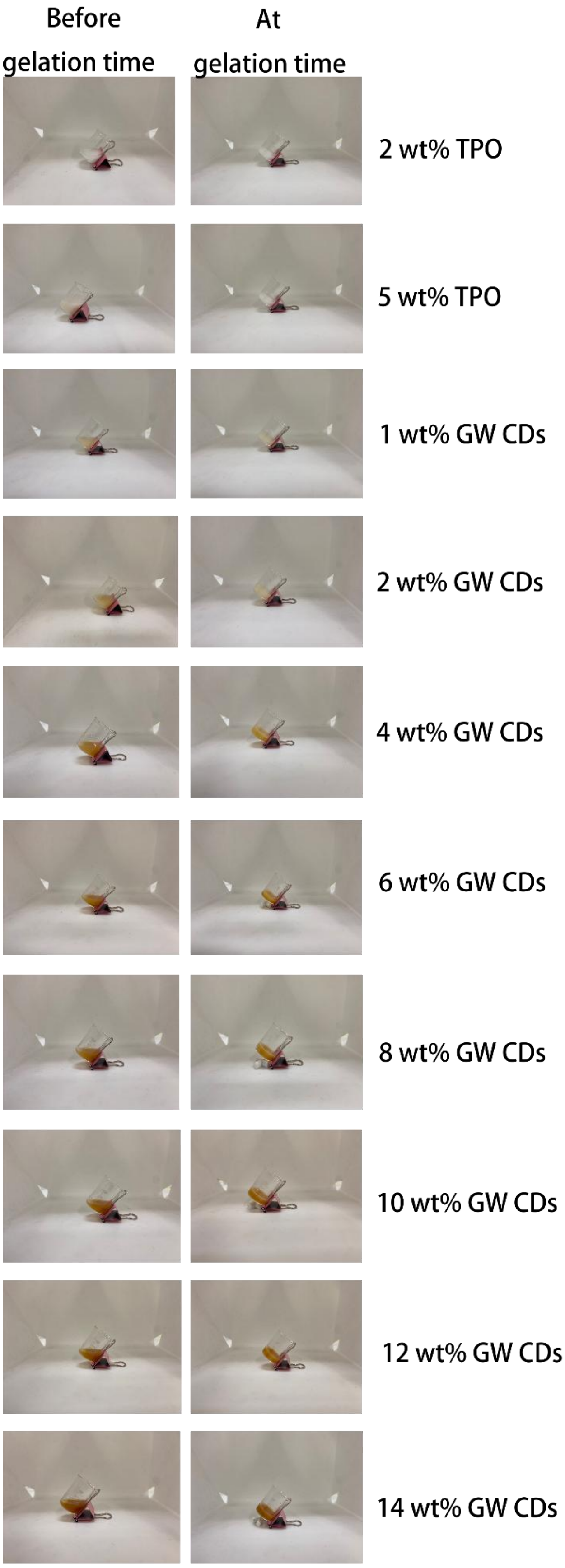

Figure S14. Images of emulsions containing various GW CDs and TPO concentrations, captured both before and at the gelation point.

Table S6. Total curing enthalpy (ΔH) measured by photo-DSC tests during PolyHIPE photocuring.

	The total curing enthalpy (ΔH) (J/g)
1% GW CDs-PolyHIPE	4.02
2% GW CDs-PolyHIPE	4.06
4% GW CDs-PolyHIPE	4.08
6% GW CDs-PolyHIPE	4.32
8% GW CDs-PolyHIPE	4.33
10% GW CDs-PolyHIPE	4.61
12% GW CDs-PolyHIPE	4.67
14% GW CDs-PolyHIPE	5.16
2% TPO-PolyHIPE	5.44
5% TPO-PolyHIPE	4.38

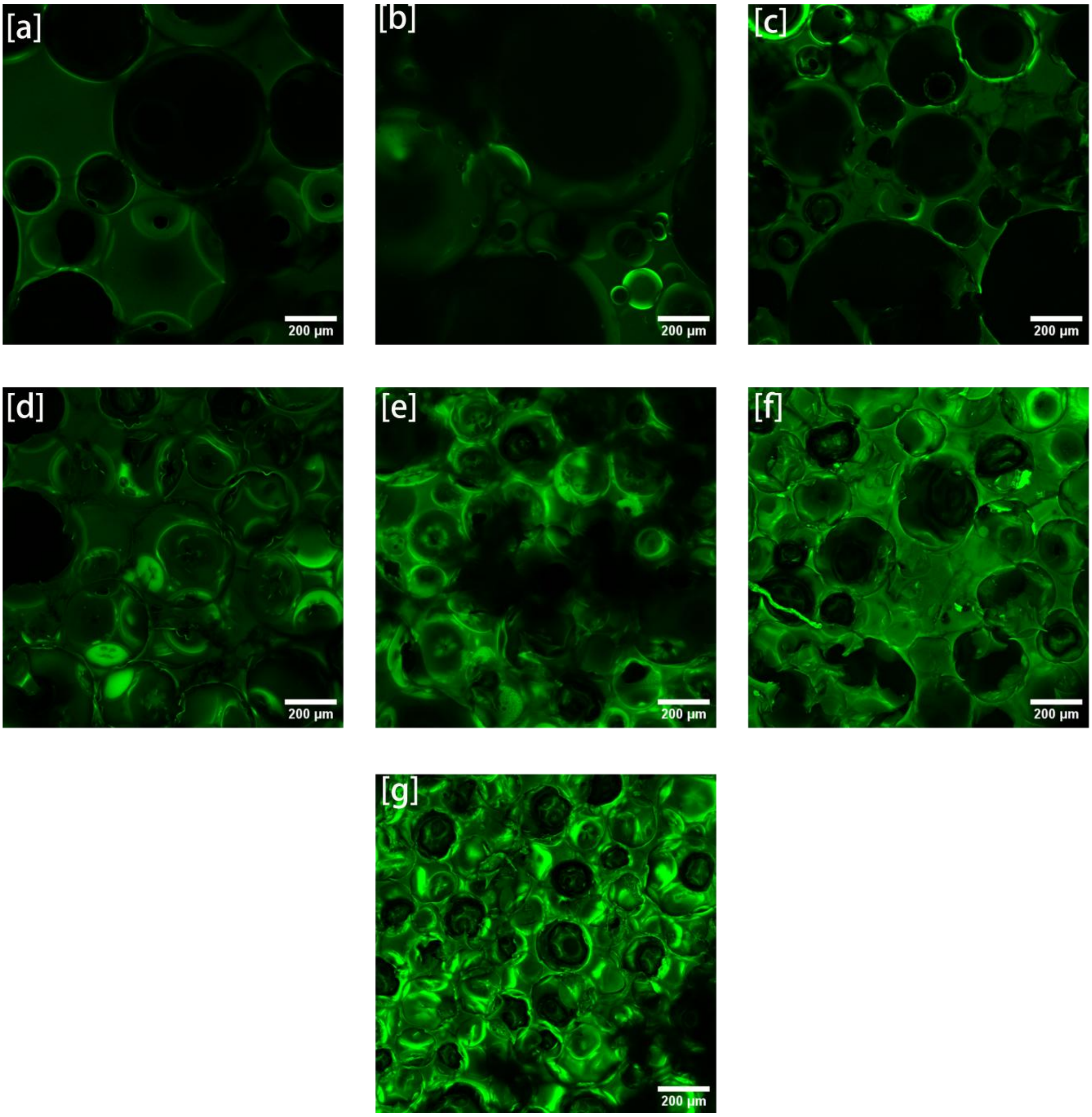

Figure S15. The confocal images of 1, 2, 4, 6, 8, 10, 12 wt% GW CDs-PolyHIPE under 488 nm excitation wavelength.

Table S7. The average droplets diameter of each GW CDs-stabilized emulsion in long-term stability test.

	The average droplets size (μm) at							
	0 min	30 min	1 h	2 h	4 h	8 h	1 day	7 days
1% GW CDs-PolyHIPE	202 ± 60	704 ± 460	creamed	-	-	-	-	-
2% GW CDs-PolyHIPE	190 ± 46	259 ± 89	672 ± 268	creamed	-	-	--	--
4% GW CDs-	171 ± 34	184 ± 56	321 ±	646 ±	creamed	-	-	-

PolyHIPE			145	183				
6% GW CDs-PolyHIPE	162 ± 37	172 ± 41	259 ± 95	481 ± 180	644 ± 346	creamed	-	--
8% GW CDs-PolyHIPE	119 ± 14	117 ± 24	174 ± 26	201 ± 39	200 ± 49	232 ± 41	529 ± 183	creamed
10% GW CDs-PolyHIPE	123 ± 11	128 ± 27	140 ± 23	149 ± 33	151 ± 33	148 ± 20	200 ± 24	240 ± 64
12% GW CDs-PolyHIPE	91 ± 14	91 ± 30	88 ± 18	90 ± 15	83 ± 12	91 ± 9	93 ± 23	113 ± 18
14% GW CDs-PolyHIPE	83 ± 13	84 ± 20	85 ± 12	83 ± 10	85 ± 8	84 ± 8	84 ± 8	105 ± 15

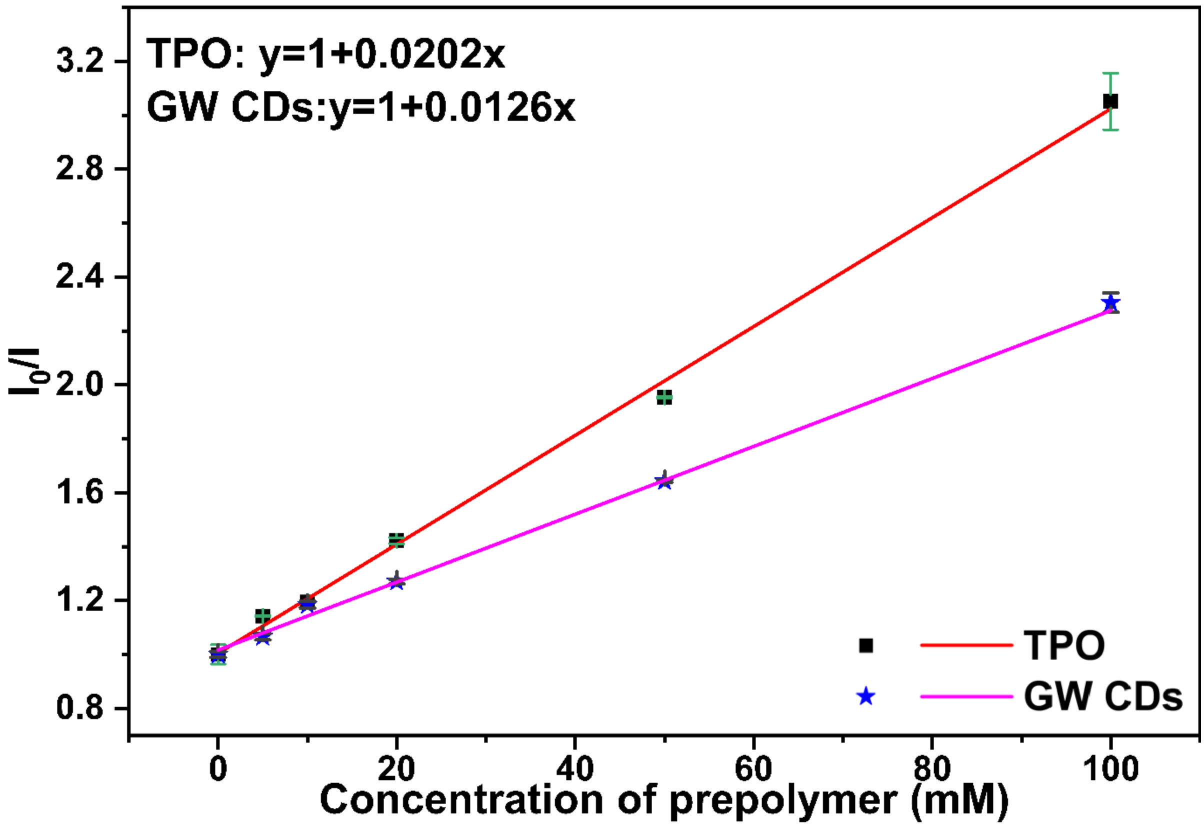

Figure S16. Stern-Volmer plots of fluorescence quenching of TPO (black squares) and GW CDs (blue stars) by the EHA/IBOA/TMPTA prepolymer mixture in ethanol.

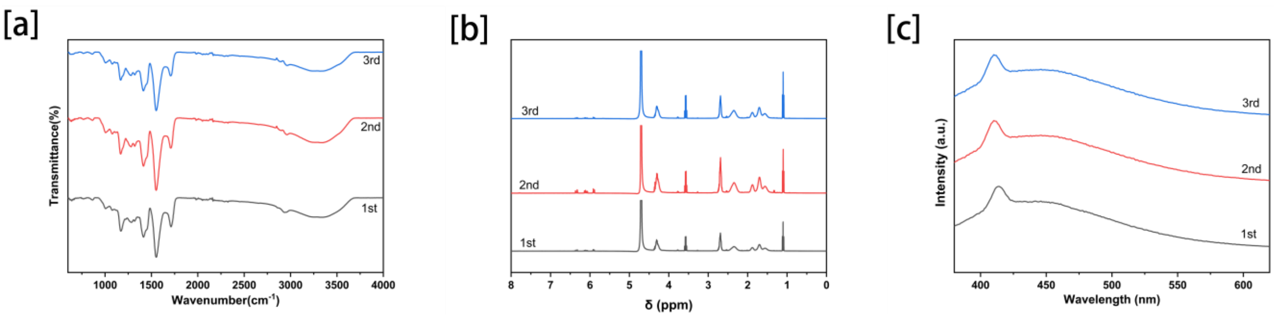

Figure S17. FTIR (a), NMR (b) and PL emission spectra (c) to test the batch-to-batch reproducibility of GW CDs prepared in three independent syntheses (1st-3rd).

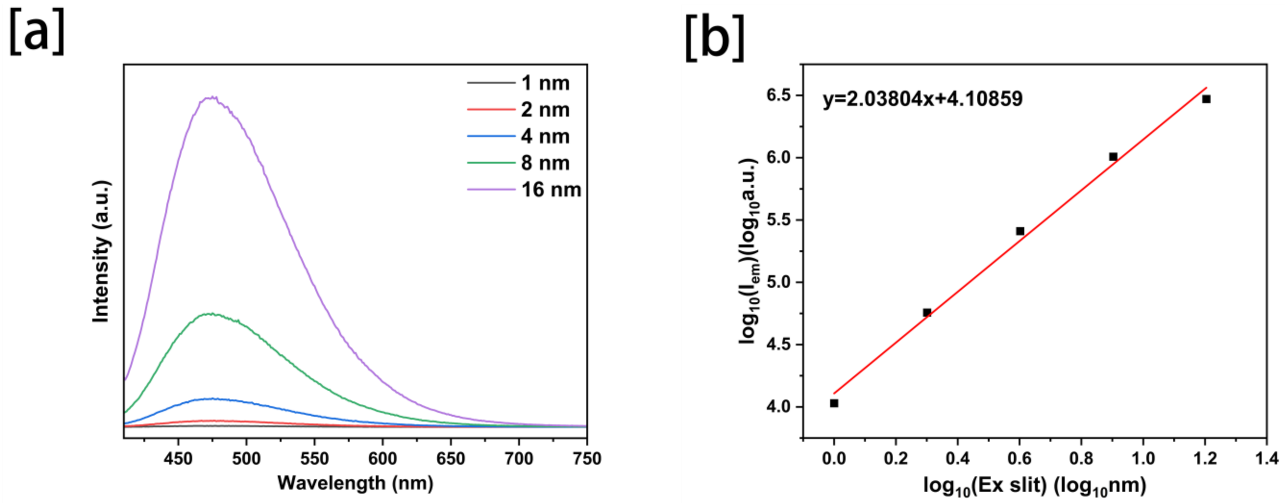

Figure S18. Influence of excitation slit width on the PL intensity of GW CDs (a) and corresponding up-conversion analysis (b).