Supporting Information for

Photocatalytic Surface Grafting of Hydrophobic Shells onto Hydrogels

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Supporting Information

Materials and Instrumentation

Materials

All chemicals were used as received unless otherwise noted. Acrylic acid (AA, > 99%), 2,2-diethoxyacetophenone (DEPO, ≥ 95%), *N*-octyl acrylate (OA, ≥ 98%), dodecyl acrylate (DA, ≥ 90%) and 1H,1H,2H,2H-heptadecafluorodecyl acrylate (HFDA, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Acridine (98%) and 1H,1H,2H,2H-perfluorooctyl acrylate (PFOA, 98%) were purchased from Energy Chemical. *N,N'*-methylene bisacrylamide (MBA) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. 2,2,6,6-Tetramethyl-1-oxylpiperidine (TEMPO, ≥98%) was purchased from Shanghai Bide Pharmatech Technology Co., Ltd. Dichloromethane (CH_2Cl_2 , A. R. grade) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Ultrapure water (ρ = 18.25 MΩ·cm) was used throughout.

Instrumentation

Fourier-Transform Infrared (FT-IR) Spectroscopy. Fourier-transform infrared (FT-IR) spectroscopy (Nicolet 5700, USA) was used to monitor the modification process of PAA hydrogel. The spectra were recorded over a wavenumber range of 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. Hydrogels were freeze-dried prior to characterization.

Scanning electron microscopy (SEM). The surface and internal morphology, as well as the elemental mapping of the pristine and encapsulated hydrogels, were characterized using SEM and energy dispersive spectroscopy (SEM-EDS, Sirion 200, The Netherlands). Hydrogels were freeze-dried and coated with Au prior to imaging and EDS analysis.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi, USA) was used to investigate the elemental compositions of the hydrogel surfaces. Hydrogels were freeze-dried prior to characterization.

Surface wettability. The surface wettability of the hydrogel surfaces during the modification process was analyzed via a contact angle measuring instrument (JC500D2, China). The average water contact angles (WCAs) were determined by conducting measurements at three different locations on a given sample.

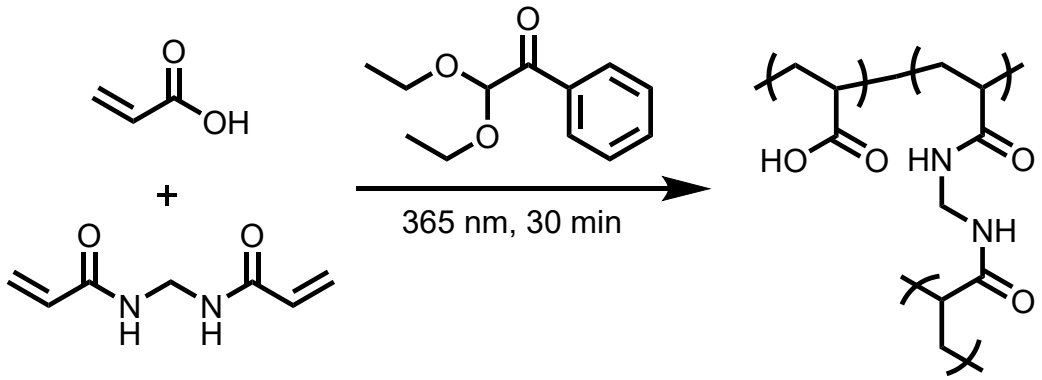
Anti-swelling behavior. The swelling processes the hydrogels were conducted by submersing the hydrogels in water at room temperature for 12 h. The anti-swelling behaviors were monitored by calculating the swelling ratio of hydrogels through the weight-measuring method using Eq. (1).

$$Swelling\ ratio = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

Here, W_t and W_0 represent the weight of the hydrogel at time *t* and 0, respectively.

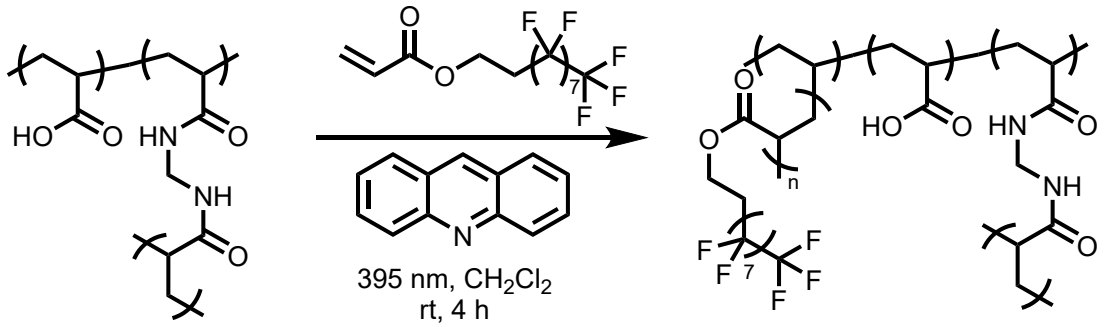
Experimental Procedures

Preparation of PAA hydrogels



AA (9.0 g, 8.57 mL, 0.12 mol, 1 equiv) was first dissolved in 30 mL of ultrapure water. MBA (0.009 g, 0.058 mmol, 0.0005 equiv) was added to 6 mL of water under vigorous stirring and subsequently added to the AA solution under stirring at room temperature. Finally, DEPO (26 μL, 26.8 μg, 0.129 mmol, 0.0011 equiv) was added to the AA/MBA solution under vigorous stirring to obtain the hydrogel precursor solution. The prepared precursor solution was then poured into a mold and irradiated under UV light (365 nm) for 30 min to form a PAA hydrogel that was sealed and stored for future use.

Surface modification of PAA hydrogels



A typical surface hydrophobization modification reaction was as follows: HFDA (0.25 g, 0.15 mL, 0.482 mmol, 1 equiv) and acridine (0.02 g, 0.112 mmol, 0.23 equiv) were dissolved in CH_2Cl_2 (10 mL) under vigorous stirring. The PAA hydrogel, left at room temperature for 3 h, was immersed in the HFDA/acridine solution. The reaction chamber was then purged with nitrogen for 3 min and stirred for 30 min. The decarboxylation modification reaction was then run for 4 h under UV light (395 nm), giving a PAA-HFDA shell-encapsulated hydrogel. A series of different PAA-HFDA and PAA-PFOA hydrogels were prepared by adjusting modification reaction time (2, 3, 4, 5, and 6 h), concentration of photocatalyst (0.001, 0.002, 0.003, and 0.004 g/mL), and concentration of hydrophobic acrylate (0.015, 0.025, 0.035, and 0.045 g/mL). A series of different PAA-OA and PAA-DA hydrogels were also prepared by adjusting the modification time, concentration of photocatalyst, and concentration of hydrophobic acrylate (0.005, 0.01, 0.015, 0.02, and 0.025 g/mL). Upon completion of the reaction, the sample surfaces were thoroughly cleaned with dichloromethane to remove residual substances.

Hydrogel Modification Reaction Optimization Results

To achieve optimal hydrophobicity, the effects of modification time, catalyst concentration, and modifier concentration on hydrogel swelling properties were investigated using a method of controlling a single variable. Firstly, the effect of modification time was investigated. Results indicated that the optimal modification time for hydrogels under different hydrophobic modifier conditions was consistently 4 h. At this point, the WCA values significantly increased while the swelling rate markedly decreased. Further prolonging the reaction time yielded limited performance improvement, suggesting surface grafting had reached saturation. Subsequently, the optimal photocatalyst concentration was determined to be 0.002 g/mL, under which the grafting reaction also reached saturation. Finally, optimal concentrations were obtained for different modifiers: DA at 0.010 g/mL, OA at 0.015 g/mL, and HFDA and PFOA at 0.025 g/mL.

Table S1: Hydrogel modification reaction optimization results

Hydrogel	Modification time (h)	[Acridine] (g/mL)	[Hydrophobic Acrylate] (g/mL)	WCA (°)
PAA-DA-1	2	0.002	0.010	88.6±1
PAA-DA-2	3	0.002	0.010	90.3±4
PAA-DA-3	4	0.002	0.010	96.8±3
PAA-DA-4	5	0.002	0.010	92.7±2
PAA-DA-5	6	0.002	0.010	92.1±5
PAA-DA-6	4	0.001	0.010	87.9±3
PAA-DA-7	4	0.003	0.010	93.4±1
PAA-DA-8	4	0.004	0.010	94.1±3
PAA-DA-9	4	0.002	0.005	97.2±3
PAA-DA-10	4	0.002	0.015	92.3±3
PAA-DA-11	4	0.002	0.020	87.9±2
PAA-DA-12	4	0.002	0.025	86.4±1
PAA-OA-1	2	0.002	0.015	115.1±2
PAA-OA-2	3	0.002	0.015	115.8±6
PAA-OA-3	4	0.002	0.015	118.3±4
PAA-OA-4	5	0.002	0.015	117.0±6
PAA-OA-5	6	0.002	0.015	116.0±4
PAA-OA-6	4	0.001	0.015	117.1±3
PAA-OA-7	4	0.003	0.015	115.9±7
PAA-OA-8	4	0.004	0.015	110.0±3
PAA-OA-9	4	0.002	0.005	113.1±4
PAA-OA-10	4	0.002	0.010	115.9±4
PAA-OA-11	4	0.002	0.015	116.8±2
PAA-OA-12	4	0.002	0.020	117.8±3
PAA-HFDA-1	2	0.002	0.025	118.4±2
PAA-HFDA-2	3	0.002	0.025	119.7±2
PAA-HFDA-3	4	0.002	0.025	128.1±1
PAA-HFDA-4	5	0.002	0.025	126.4±2
PAA-HFDA-5	6	0.002	0.025	126.3±4
PAA-HFDA-6	4	0.001	0.025	123.3±3

PAA-HFDA-7	4	0.003	0.025	124.2±1
PAA-HFDA-8	4	0.004	0.025	122.3±2
PAA-HFDA-9	4	0.002	0.015	121.0±2
PAA-HFDA-10	4	0.002	0.035	123.9±1
PAA-HFDA-11	4	0.002	0.045	121.6±3
PAA-PFOA-1	2	0.002	0.025	120.1±1
PAA-PFOA-2	3	0.002	0.025	123.1±6
PAA-PFOA-3	4	0.002	0.025	128.3±2
PAA-PFOA-4	5	0.002	0.025	122.0±2
PAA-PFOA-5	6	0.002	0.025	122.3±1
PAA-PFOA-6	4	0.001	0.025	121.4±3
PAA-PFOA-7	4	0.003	0.025	117.6±5
PAA-PFOA-8	4	0.004	0.025	117.8±6
PAA-PFOA-9	4	0.002	0.015	114.4±3
PAA-PFOA-10	4	0.002	0.035	120.1±3
PAA-PFOA-11	4	0.002	0.045	120.3±4

Water Contact Angles (WCAs) and Swelling Ratios of Hydrogels vs. Modification Time

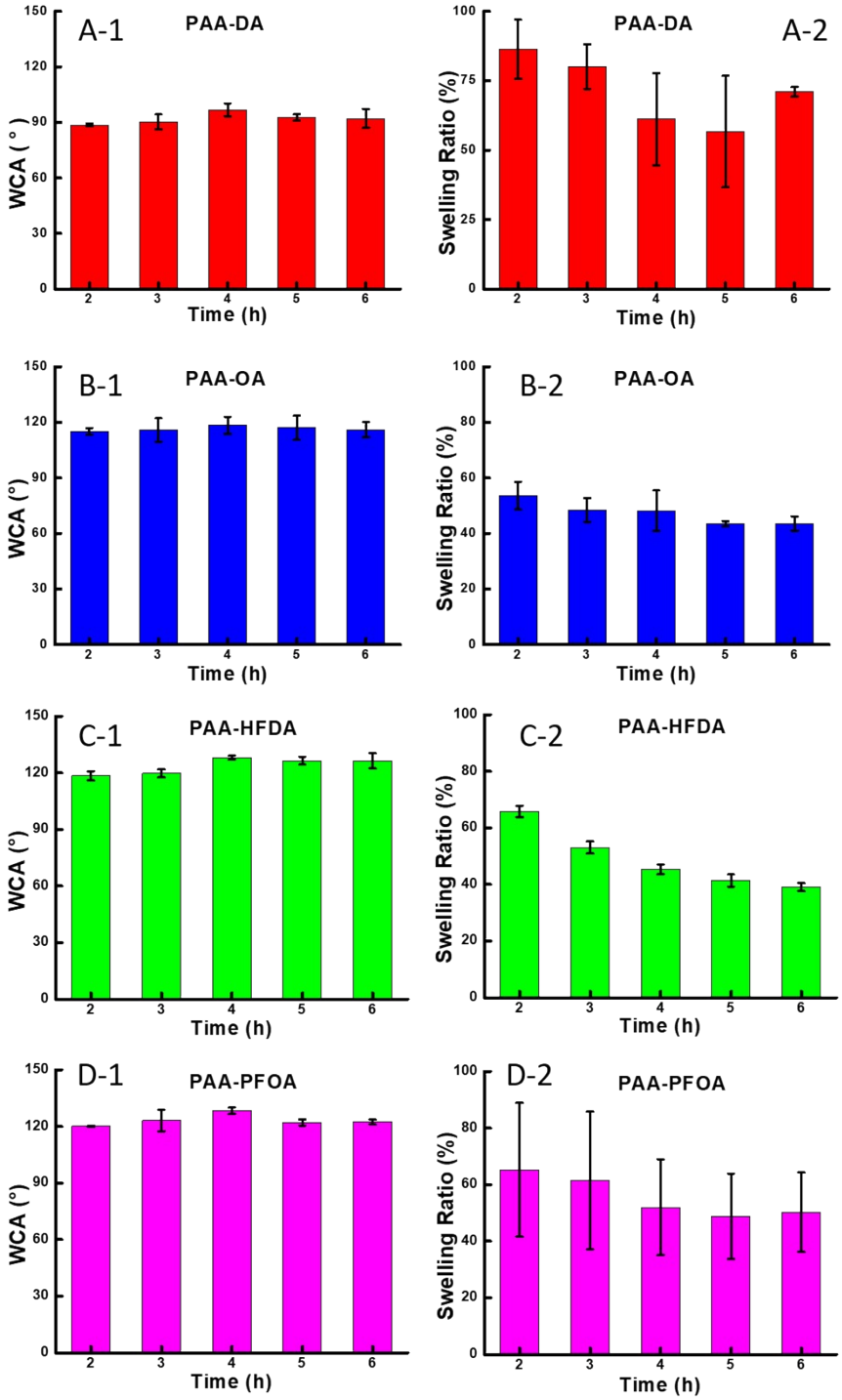


Fig. S1. Water contact angles (WCA, A-1–D-1) and swelling ratios (A-2–D-2) of the modified hydrogels with different modification times. (A-1, A-2): PAA-DA hydrogel, (B-1, B-2): PAA-OA hydrogel, (C-1, C-2): PAA-HFDA hydrogel, (D-1, D-2): PAA-PFOA hydrogel.

WCAs and Swelling Ratios of Hydrogels vs. Photocatalyst Concentration

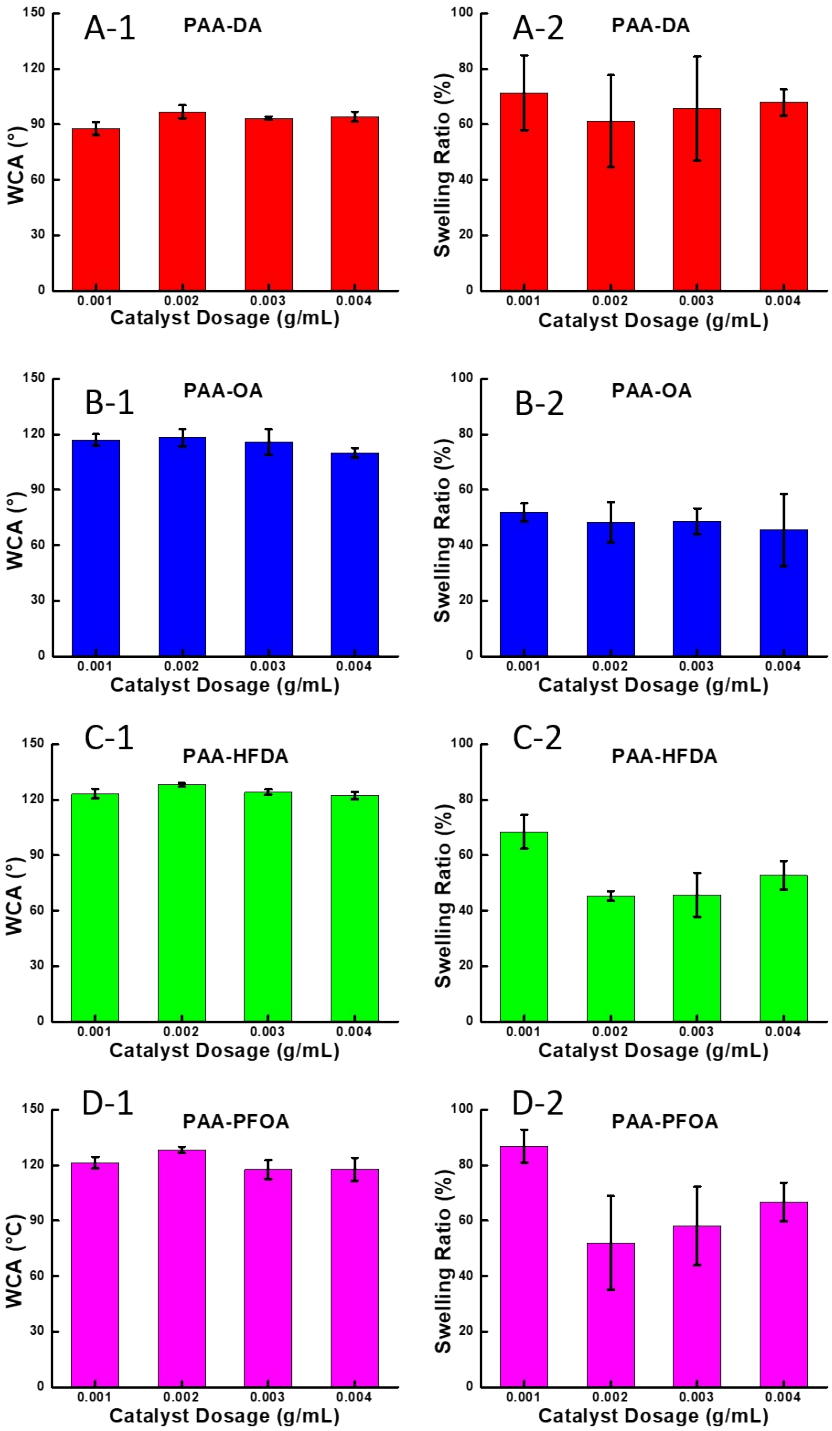


Fig. S2. WCAs (A-1–D-1) and swelling ratios (A-2–D-2) of the modified hydrogels with different concentrations of photocatalyst. (A-1, A-2): PAA-DA hydrogel, (B-1, B-2): PAA-OA hydrogel, (C-1, C-2): PAA-HFDA hydrogel, (D-1, D-2): PAA-PFOA hydrogel.

WCAs and Swelling Ratios of Hydrogels vs. Hydrophobic Acrylate Concentration

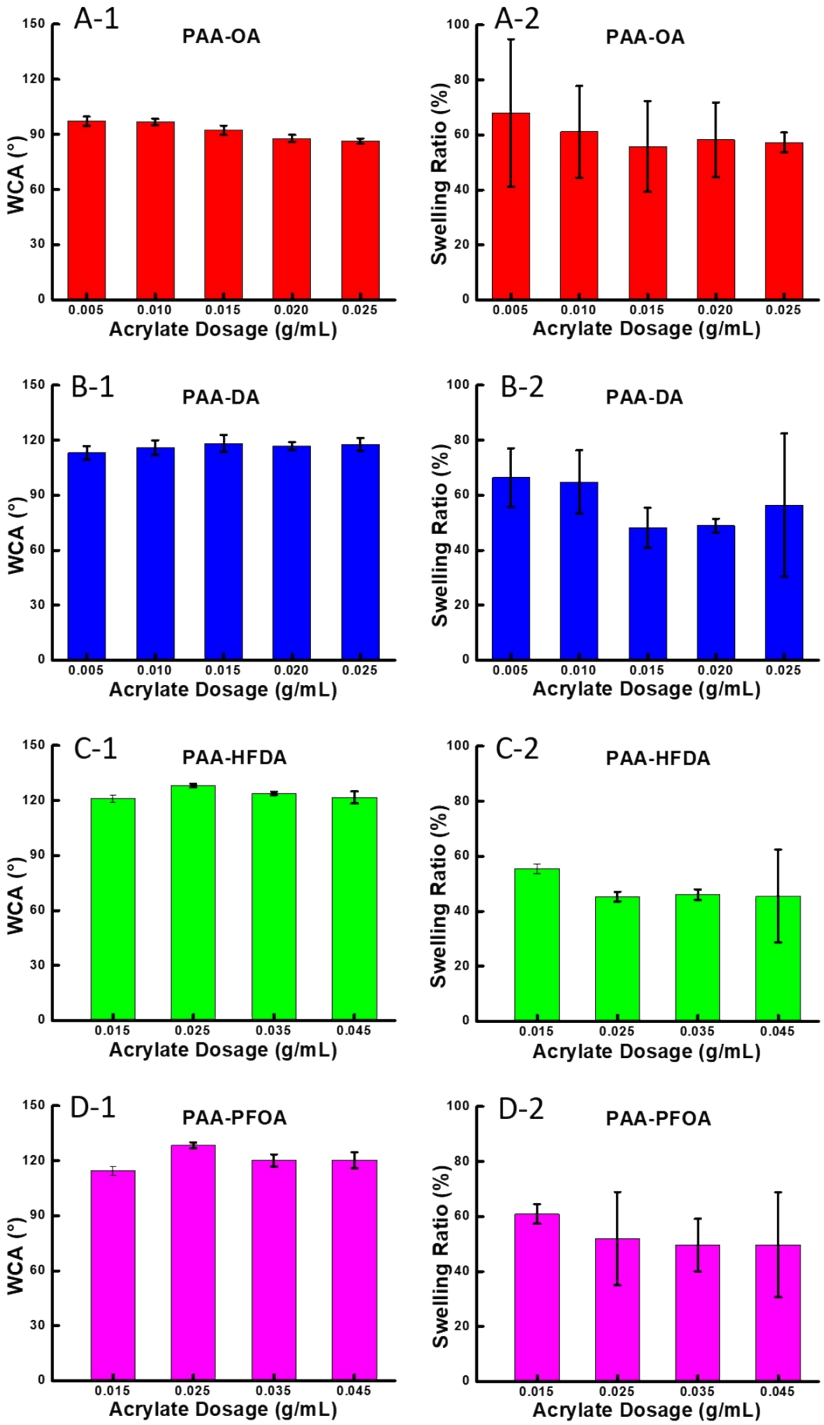


Fig. S3. WCAs (A-1–D-1) and swelling ratios (A-2–D-2) of the modified hydrogels with different concentrations of hydrophobic acrylate. (A-1, A-2): PAA-DA hydrogel, (B-1, B-2): PAA-OA hydrogel, (C-1, C-2): PAA-HFDA hydrogel, (D-1, D-2): PAA-PFOA hydrogel.

Control Experiments

To further verify that the hydrophobic modifier was chemically grafted onto the hydrogel surface, control experiments were conducted for validation. Following the above mentioned PAA hydrogel surface modification procedure, we performed the following experiments: (1) removing only the hydrophobic modifier (HFDA), (2) eliminating only the UV light, (3) excluding only the photocatalyst (acridine). Consequently, comparison samples without the hydrophobic modifier, without UV light, or without the photocatalyst were obtained.

Results showed that only removing the HFDA modifier resulted in a WCA value of 31.4 ± 7° (Fig. S4 and Table S2), which was comparable to the WCA of the unmodified hydrogel. This indicates that HFDA plays an indispensable key role in surface modification of the gel. Subsequently, PAA hydrogels were modified under identical conditions without UV light activation or without the addition of the photocatalyst. The WCA values of the resultant hydrogel surfaces were only 67.6 ± 4° and 59.5 ± 7°, respectively (Fig. S4 and Table S2). Despite exceeding the value of the unmodified hydrogel (37.9 ± 6°), these values remained significantly lower than that of the PAA-HFDA hydrogel (128.1 ± 1°) (Fig. S4 and Table S2). This indicates that the reaction involved only slight adsorption rather than complete surface adsorption, while also confirming the occurrence of a chemical reaction triggered by UV light.

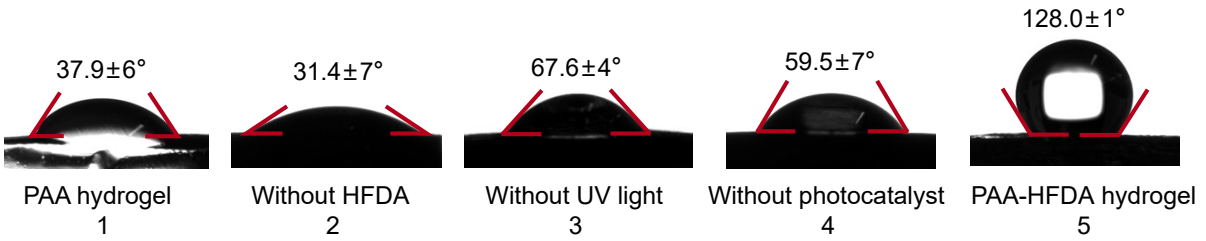


Fig. S4. Photos of water droplets on the surface of the resultant hydrogels after control experiments.

Table S2: Reaction conditions for the control experiments and WCAs of the resultant hydrogel surfaces

Condition Number	Irradiation time of UV Light (h)	[Acridine] (g/mL)	[HFDA] (g/mL)	WCA (°)
Control-1	-	-	-	37.9±6
Control-2	4	0.002	-	31.4±7
Control-3	-	0.002	0.025	67.6±4
Control-4	4	-	0.025	59.5±7
Control-5	4	0.002	0.025	128.0±1

Radical Trapping Experiment

Meanwhile, to obtain more direct evidence of the hydrophobic modifier being chemically grafted onto the hydrogel surface, radical trapping experiments were conducted for validation. Following the above mentioned PAA hydrogel surface modification procedure, we performed the following experiments: (1) UV light irradiation with both HFDA/acridine and the radical trapper TEMPO, (2) UV light irradiation with TEMPO and acridine, (3) with TEMPO and acridine but without UV light, (4) UV light irradiation with only TEMPO.

Results indicated that when radical trapper TEMPO was added to the reaction system and UV light irradiated, the surface WCA value of the resultant hydrogel was 94.8 ± 3°(Fig. S5 and Table S3), which was significantly lower than that of the PAA-HFDA hydrogel. When the reaction system contained TEMPO but no HFDA, the WCA value turned to 84.7 ± 5°(Fig. S5 and Table S3). Both values were lower than that of the PAA-HFDA hydrogel but higher than that of the pure PAA hydrogel. This was because that TEMPO captured the free radicals generated on the surface of the hydrogel network during the modification process and chemically grafting them onto the hydrogel surface. When only TEMPO was present, the WCA values of the resultant hydrogel under conditions of only photocatalyst or only UV light were 53.1±8° and 58.7±8°(Fig. S5 and Table S3), respectively. This clearly indicated only minimal adsorption occurred during the reaction and confirmed the radical generation. The presence of TEMPO inhibited the chemical reaction between radicals and HFDA, further substantiating that chemical modification took place. Consequently, this experiment provides compelling evidence that the observed alteration in surface properties resulted from chemical graft polymerisation rather than purely physical adsorption.

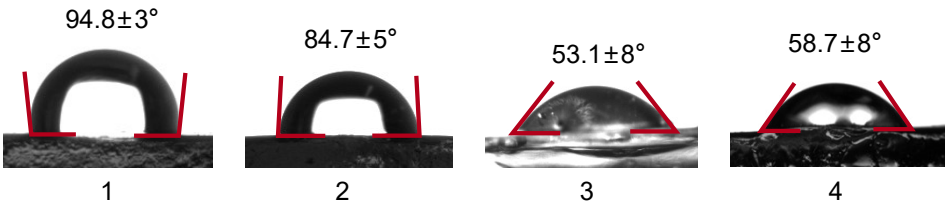


Fig. S5. Photos of water droplets on the surface of the resultant hydrogels after radical trapping experiments.

Table S3: Reaction conditions for the radical trapping experiment and WCAs of the resultant hydrogel surfaces

Condition Number	Irradiation time of UV Light (h)	[Acridine] (g/mL)	[HFDA] (g/mL)	[TEMPO] (g/mL)	WCA (°)
Radical Trapping-1	4	0.002	0.025	0.011	94.8±3
Radical Trapping-2	4	0.002	-	0.011	84.7±5
Radical Trapping-3	-	0.002	-	0.011	53.1±8
Radical Trapping-4	4	-	-	0.011	58.7±8

Photomask Experiment

To validate light-induced surface chemical grafting, photomask experiments were conducted for validation. However, the mask could not adhere to the hydrogel surface in CH_2Cl_2. And due to the exceptional penetrating power of UV light, achieving precise spatial control over the reaction area on the solid-liquid interface during in situ photomasking proved challenging. Consequently, the experimental protocol was adjusted as follows: HFDA (0.25 g, 0.15 mL, 0.482 mmol) and acridine (0.02 g, 0.112 mmol) were dissolved in CH_2Cl_2 (10 mL) under vigorous stirring. The PAA hydrogel, which had been left at room temperature for 3 h, was placed in the prepared solution and soaked for 4 h. The PAA gel was then retrieved, with one half exposed to UV light while the other remained shielded. The reaction proceeded for 2 h. Upon reaction completion, all samples were washed thoroughly with excess CH_2Cl_2.

A marked contrast was evident between the exposed surface and the regions shielded by the photomask, both visually and in wettability. Significant color differences were observed between the exposed and photomask-shielded regions. Contact angle measurements, taken at specific points within these patterned areas, yielded values of 128.0° ± 1° (exposed) and 67.6° ± 4° (shielded) (Fig. S6). This localized property contrast cannot be explained by uniform physical adsorption and is definitively attributed to the formation of a covalently bonded hydrophobic layer. Instead, it confirms that the hydrophobic surface layer is chemically grafted onto the hydrogel.

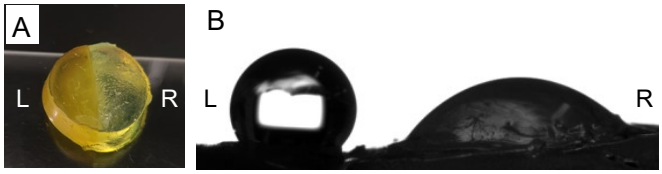


Fig. S6. (A) Photo comparison of hydrogel with (L) and without (R) UV irradiation. (B) The WCA diagrams of the hydrogel in the UV-irradiated area (L) versus the non-UV-irradiated area (R).

High-Resolution XPS Traces

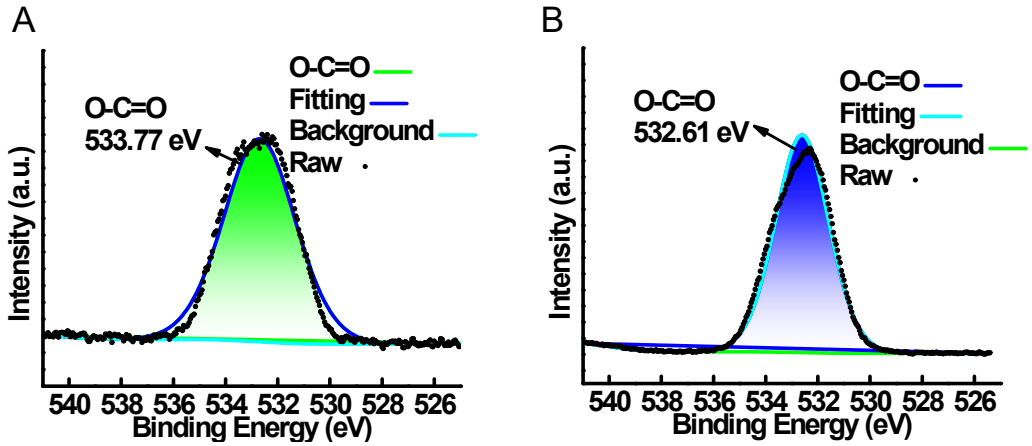


Fig. S7. High-resolution X-ray photoelectron spectroscopy (XPS) spectra with fitting curves of O 1s region characteristic for the (A) poly(acrylic acid)-1H,1H,2H,2H-heptadecafluorodecyl acrylate (PAA-HFDA) hydrogel and (B) pristine PAA hydrogel.

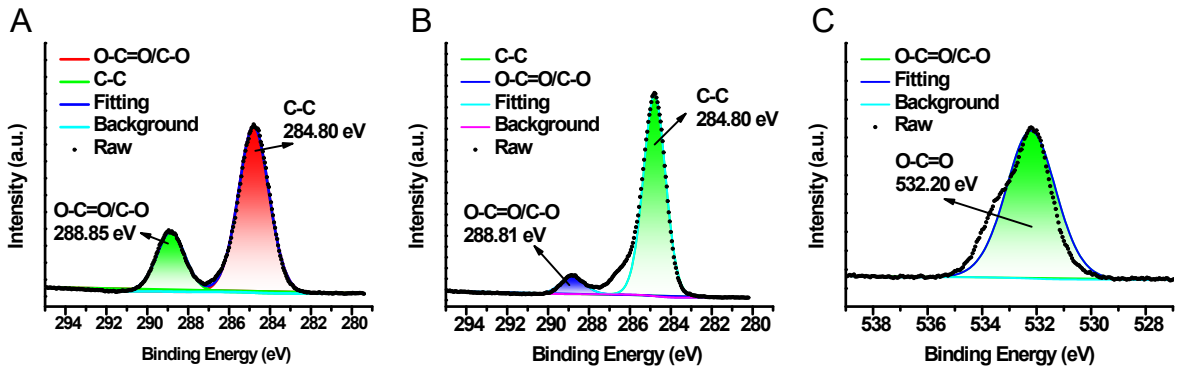


Fig. S8. High-resolution XPS spectra with fitting curves of the C 1s region characteristic for the (A) PAA hydrogel and (B) PAA-*n*-octyl acrylate (PAA-OA) hydrogels. (C) O 1s region characteristic for the PAA-OA hydrogel.

X-ray Photoelectron Spectroscopy (XPS) Elemental Percentage Results

Table S4: X-ray photoelectron spectroscopy (XPS) results of unencapsulated hydrogels and hydrophobic, shell-encapsulated hydrogels

Elementals	C (%)	O (%)	F (%)
PAA	62.07	34.97	/
PAA-HFDA	40.97	6.4	51.92
PAA-OA	77.2	16.78	/

Images of Hydrogels Before and After Modification

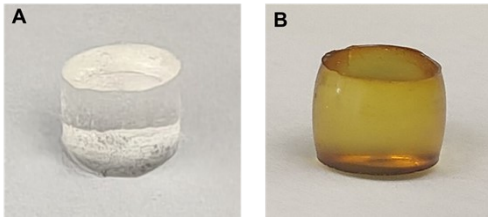


Fig. S9. (A) Photo of the unencapsulated hydrogel. (B) Photo of hydrogel encapsulated by hydrophobic shell.

Scanning Electron Microscopy (SEM) Images and Elemental Mapping of Hydrogels

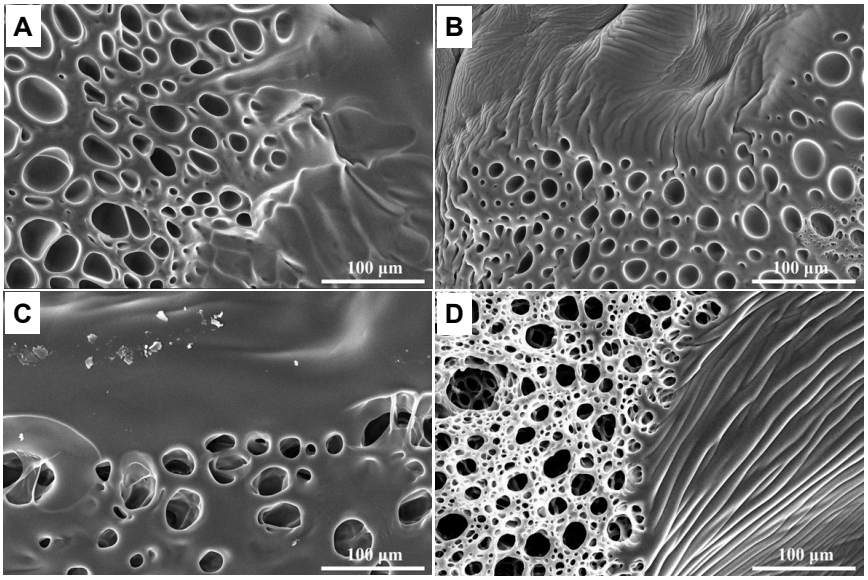


Fig. S10. Scanning electron microscopy (SEM) images of the cross sections of the hydrogels: (A) PAA-DA, (B) PAA-OA, (C) PAA-HFDA, and (D) AA-PFOA.

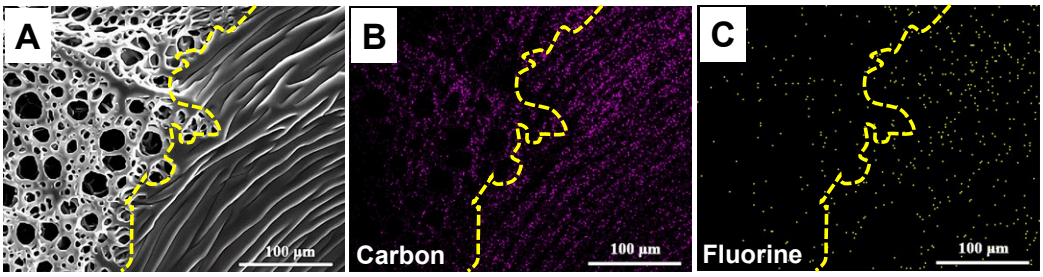


Fig. S11. (A) SEM image of the cross-section of PAA-PFOA. (B)-(C) Elemental mapping in the cross section of PAA-PFOA: (B) carbon elemental; (C) fluorine elemental.