Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Photopolymerized superhydrophobic hybrid coating enabled by dual-purpose tetrapodal ZnO for liquid/liquid separation

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1. General Information

Methyl methacrylate (MMA) and n-butyl methacrylate (BMA) containing 10 ppm photopolymerization inhibitor Mequinol (MEHQ) were purchased from Electron Microscopy Sciences and used as received without removing MEHQ. n-Lauryl methacrylate (LMA) containing 500 ppm MEHQ and Span 80 was purchased from Sigma Aldrich and used as received without removing MEHQ. Methanol and 2-propanol (IPA) were purchased from Fisher Scientific. 99% Zinc plates with the thickness of 0.51 mm and stainless steel meshes with the opening size of 109 µm were obtained from Mcmaster-Carr. Zinc oxide nanoparticles were purchased from Spectrum Chemical Manufacturing Corporation. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was provided by Combi Blocks. 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][TFSI]) were purchased from IoLiTech. High-density polyethylene (HDPE) with a melting temperature of 132 °C was supplied by Formosa Plastics Corporation. Polylactic acid (PLA) filament with a glass transition temperature of 60 °C was purchased from Sunlu Industrial Corporation. All materials were used as received without further purification.

^{1}H Nuclear Magnetic Resonance (NMR) spectra were obtained using Bruker Avance Neo 400 MHz spectrometers at room temperature. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker ELEXSYS II E500 with the microwave frequency of ca. 9.356 GHz at ambient temperature. Static water contact angles were measured on a KSV CAM200 optical goniometer. A manual micropipette was used to release distilled water or hexadecane droplets with an average size of 5 µL. In the sliding angle tests, the average droplet size was set as 20 µL. All reported contact angles in this work are average numbers of at least five values measured on different positions of the samples. Water sliding angles were measured with the help of a rotating sample stage. Dynamic viscosities of liquids were determined by a TA instrument ARES-G2 rotational rheometer at 25 °C.

2. Methods

Synthesis of ZnO Tetrapods: ZnO tetrapods were prepared by oxidizing metallic Zn in air through a slightly modified procedure based on a previously reported method.[1] Briefly, 10 g of Zn metal was cut into small pieces with a size of around 1 cm × 0.5 cm and placed on a quartz boat. The boat was subsequently inserted into a 3-inch-diameter quartz tube in a tube furnace that had been preheated to 940 °C. After holding the temperature for 2 min, ZnO tetrapods formed on the inner wall of the quartz tube, subsequently were collected and dispersed in isopropyl alcohol (IPA) with a concentration of 20 mg/ml.

Fabrication of Polymer/T-ZnO-Coated Substrates: The ZnO/IPA suspension (20 mg/ml) was spray-coated onto a horizontally placed stainless-steel mesh, quantitative filter paper (particle retention:1 μm), HDPE or PLA substrate using an airbrush with a nozzle diameter of 0.5 mm at 1 bar until a coating density of 3.5 mg/cm^2 (14 mg/cm^2 for filter paper) was reached. The coated mesh was then dipped into a solution of monomer in IPA [50% (v/v)] in a glass petri dish. The amount of solution used was 0.5 ml per cm^2 of the mesh. Subsequently, UV irradiation of 100 mW/cm^2 was applied to the immersed mesh using a 365 nm LED light source for a certain time. For the large-area coating, 10 mW/cm^2 UV light was applied to the surface for 9 h. The resulted polymer/ZnO mesh was washed with methanol thoroughly. The coated mesh was ready for characterization and test after being dried in dark at ambient condition for 12 h.

Figure S1. Experimental setup for a 30 × 60 cm mesh coating

Fabrication of smooth polymers: poly(methyl methacrylate) (PMMA), poly(butyl methacrylate) (PBMA) and poly(lauryl methacrylate) (PLMA) synthesized via T-ZnO initiated bulk photopolymerization was heated to 200 °C and coated onto a clean and smooth glass substrate, using a doctor blade, respectively.

Liquid/liquid Separation: As the filtration layer, a ZnO-PLMA-40 mesh was placed in between the two components of a glass Busch funnel fixed by a clamp. Oils were dyed with Oil O Red and aqueous solutions were dyed with Brilliant Blue R. In a typical test, liquid/liquid mixtures (50%, v/v) were poured into the separator with a tilted angle of around 55°. For the separation of ionic liquid C6MImNTf$_2$ and water, the separator was placed vertically due to the higher density of the ionic liquid. The permeate flux *F* was determined by using the following equation:

$$F = V / St \tag{1}$$

where V is the volume of oil that permeates through the mesh, S represents the effective cross-sectional area of the mesh and t refers to the time required for the permeation. The separation efficiency η was calculated according to the following equation:

$$\eta = (m_1 / m_0) \times 100\% \tag{2}$$

Where m_0 and m_1 are the mass of the liquids rejected by the mesh before and after the separation, respectively. The intrusion pressure P_{int} can be derived by the following equation:

$$P_{\text{int}} = \rho g h_{\text{max}} \tag{3}$$

where ρ refers to the density of water, g is the acceleration of gravity and h_{max} represents the maximum water column height. Theoretical intrusion pressure $P_{\text{int, theor}}$ of the mesh was calculated by using the following equation:

$$P_{\text{int, theor}} \sim 2\gamma \cos\theta / d \tag{4}$$

where γ is the surface tension of water, θ denotes the water contact angle, and d refers to the diameter of the pores.

Emulsion Separation: Water-in-oil emulsion was prepared by mixing water with hexane at a ratio of 1:100 (v/v) with 2 mg/ml Span 80 as the surfactant, followed by being stirred extensively for 4 h. The as-prepared emulsion is stable for at least 3 days without demulsification. In the separation, the sample membrane was fixed in an standard vacuum filtration setup. The emulsion was poured on top and separated under mild vacuum pressure (~0.03MPa). The feed emulsion and filtrate were collected and the droplet sizes were characterized by optical microscopy and dynamic light scattering measurements.

Durability Tests: Mechanical durability of the prepared samples was examined in two types of tests that simulate the situations in practical liquid/liquid separation applications:[2] (1) water spray impact test and (2) droplet impact test. Distilled water was used for both examinations. In the water spray test, an airbrush with a nozzle diameter of 0.5 mm was used to spray water vertically onto a horizontally placed sample. The pressure of the air compressor was set as 4 bar and the nozzle was moved horizontally at a speed of about 4 cm/s while maintaining 7.5 cm away from the surface. After the whole surface was covered, a new cycle started. In this test, water spray impacted the surface with a speed of 3.8 m/s and a pressure of 3.4 kPa. In the droplet impact test, water droplets were released from a funnel at a height of 30 cm at a rate of 2 droplets/s to impact the substrate at a 45° tilted angle. The resulted impact speed was 2.4 m/s, corresponding to an impact pressure of 2.9 kPa. Chemical durability of the coated meshes was tested by measuring the static contact angles of aqueous solutions of 1M NaOH, 1M HCl and 1M NaCl in lieu of water. UV durability of the samples was evaluated by the changes in their static water contact angles on exposure to UV light (1 mW/cm^2) for a certain time.

3. NMR Spectra

To evaluate the reaction efficiency of T-ZnO-initiated photo-polymerization, ^{1}H NMR was utilized to determine the monomer conversion in the solution after reaction. Specifically, a 3.5 cm × 3.5 cm mesh coated with ZnO (3.5 mg/cm^2) was soaked into the monomer/IPA solution (6 ml, 50% v/v). After UV irradiation (100 mW/cm^2), the reaction was quenched by bubbling air to the solution for 5 min. The entire reaction mixture, including the residual solution and the surface coated polymer, was dissolved, dried, and subjected to ^{1}H NMR spectroscopy (Figure S1). The monomer conversion α was calculated based on the ratio of unreacted monomer concentration and the original total monomer concentration, according to the following equation:

$$\alpha = \left(1 - \frac{I_{\mathrm{f}} + I_{\mathrm{g}}}{I_{\mathrm{d,d'}}}\right) \times 100\%$$

Whereas I_{f} and I_{g} correspond to the NMR integration values of proton signals *f* and *g* in the unreacted monomer, respectively; while I_{d} and $I_{\mathrm{d'}}$ correspond to the NMR integration values of overlapped proton signals *d* and *d'* in the unreacted monomer and the reacted polymer.

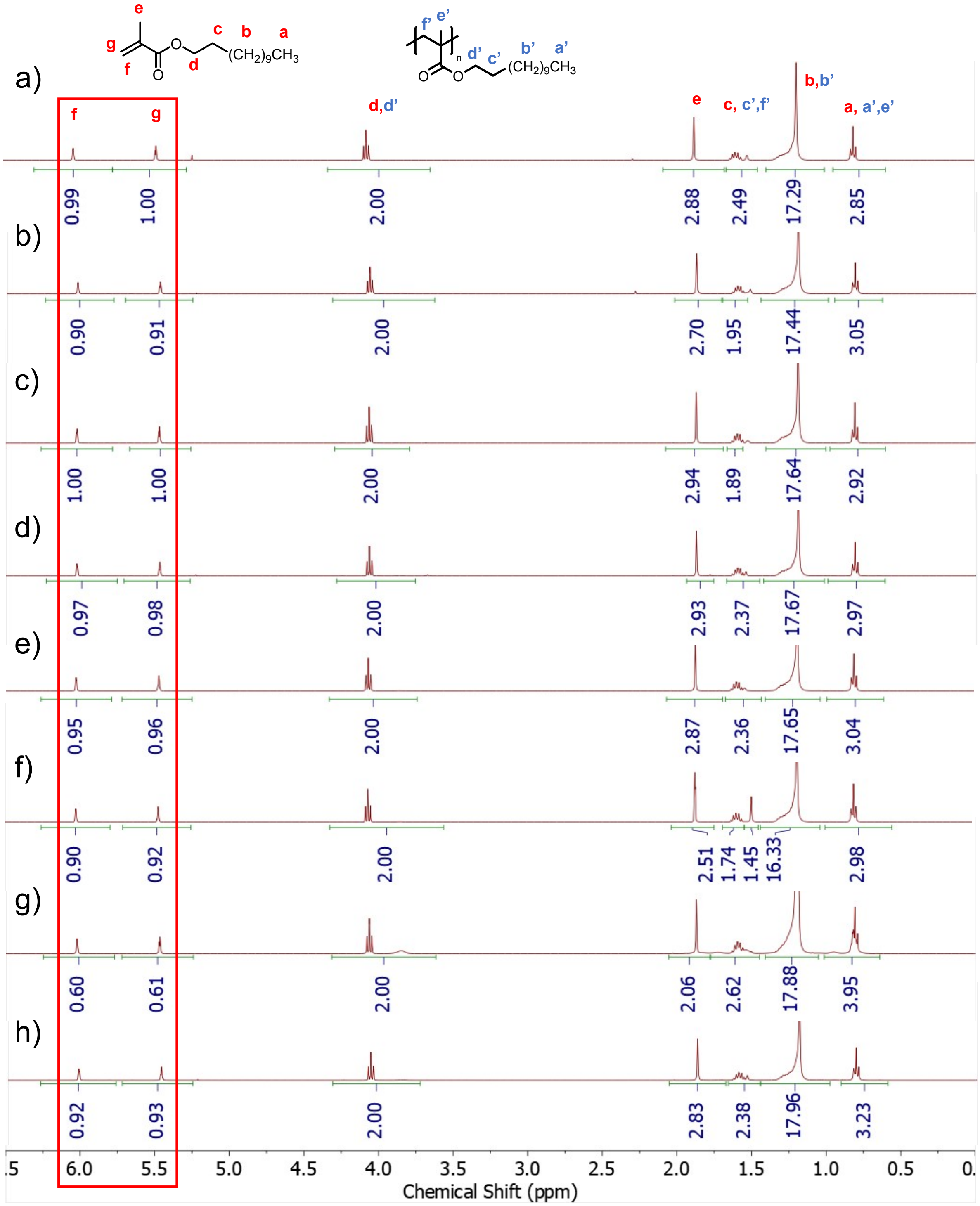

Figure S2. a)-h): ^{1}HNMR spectra of the final solutions of Entries 1-8.

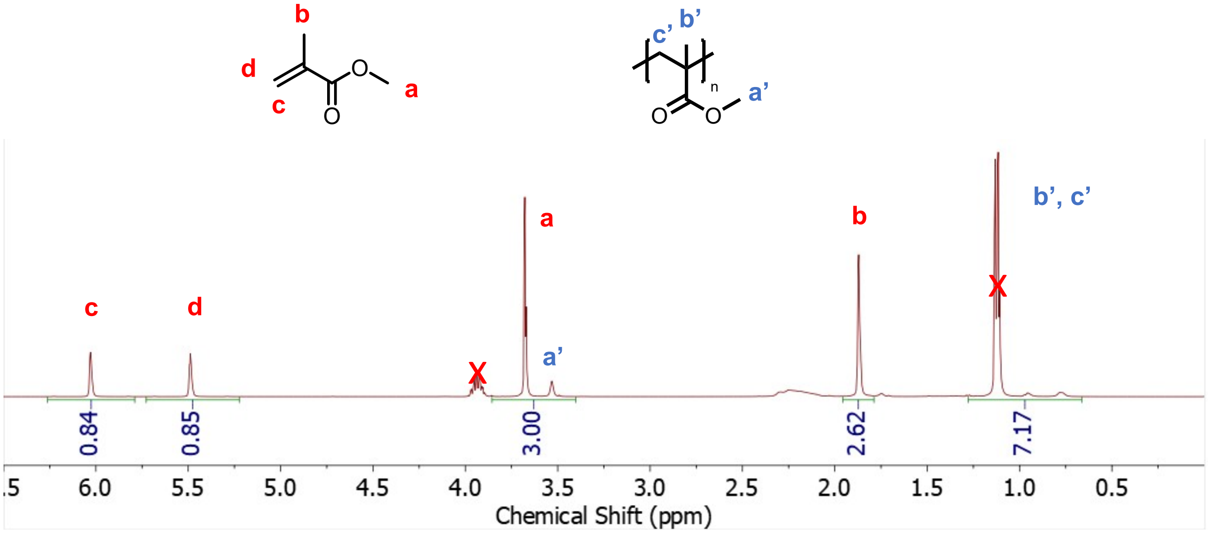

Figure S3. ^{1}HNMR spectrum of the final solution of Entry 9.

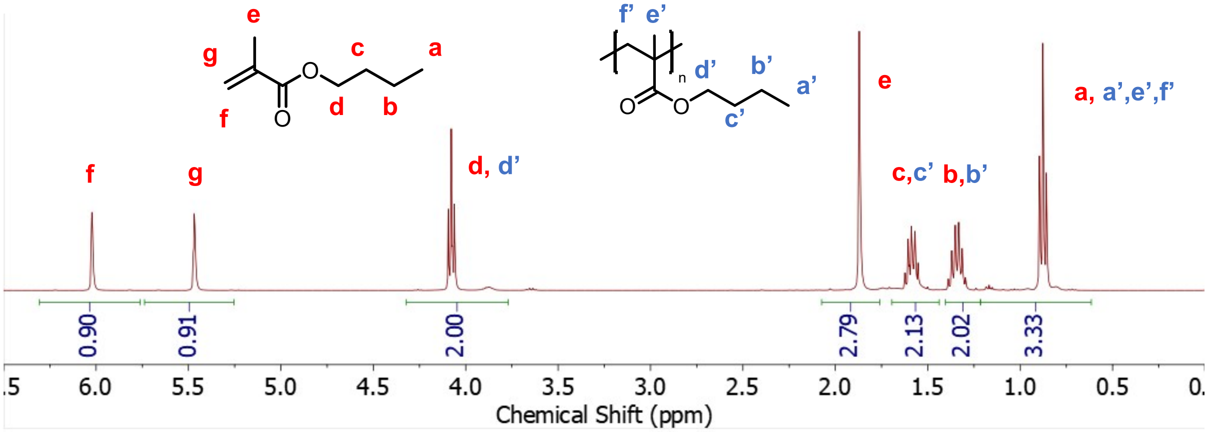

Figure S4. ^{1}HNMR spectrum of the final solution of Entry 10.

4. Thermogravimetric Analysis (TGA)

Weight fractions of polymers in the ZnO/polymer composites were measured by TGA data. The surface-coated hybrid of polymer and T-ZnO on stainless-steel mesh was digested and suspended with CH_2Cl_2. The suspension was casted on a glass substrate and then left for dry before it was transferred into an alumina crucible for TGA. TGA data were collected on a TA instrument Q500 thermogravimetric analyzer at a heating rate of 20 °C min^{-1} from 30 °C to 700 °C under nitrogen atmosphere.

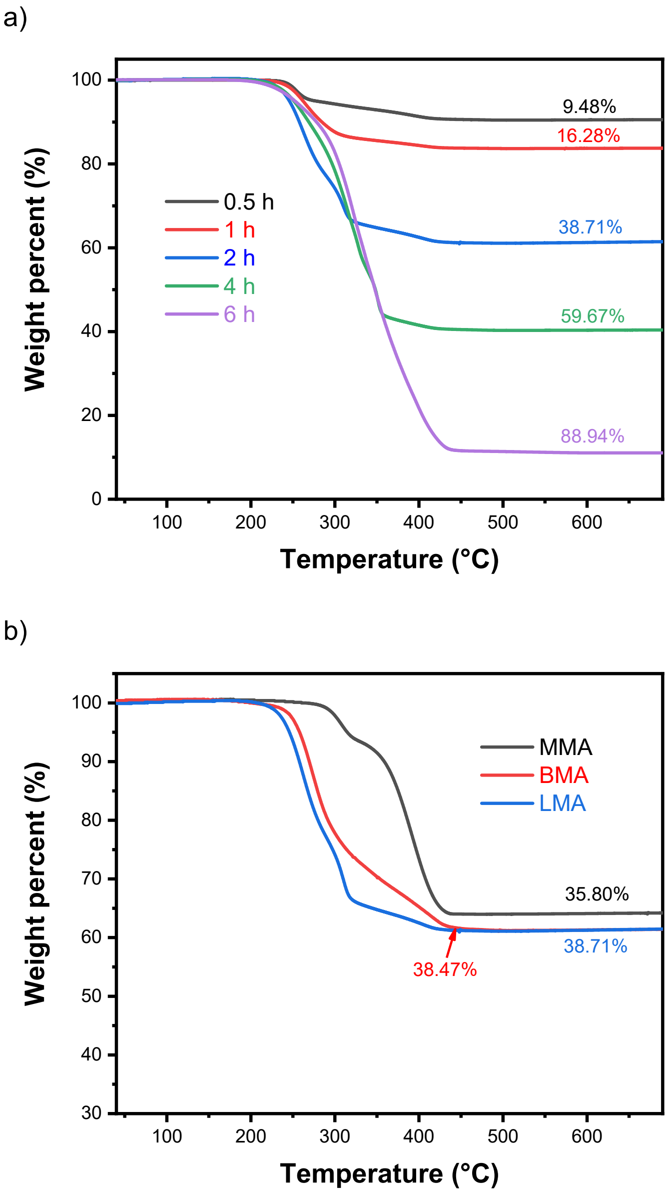

Figure S5. TGA plots of (a) T-ZnO/PLMA composites after different UV irradiation time and, the percentage number refers to the weight fraction of polymer in the hybrid; and (b) T-ZnO composites with different polymers (PMMA, PBMA and PLMA).

5. Size Exclusion Chromatography (SEC)

SEC measurements were performed with THF as eluent on a Tosoh HLC-8320 EcoSEC instrument. The molar masses were calculated using a calibration curve derived from the refractive index peaks of polystyrene standard samples.

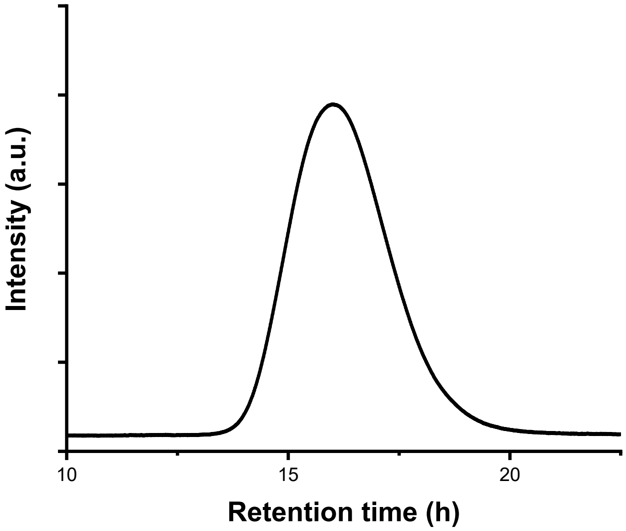

Figure S6. Size exclusion chromatogram of the polymer obtained in Entry 2.

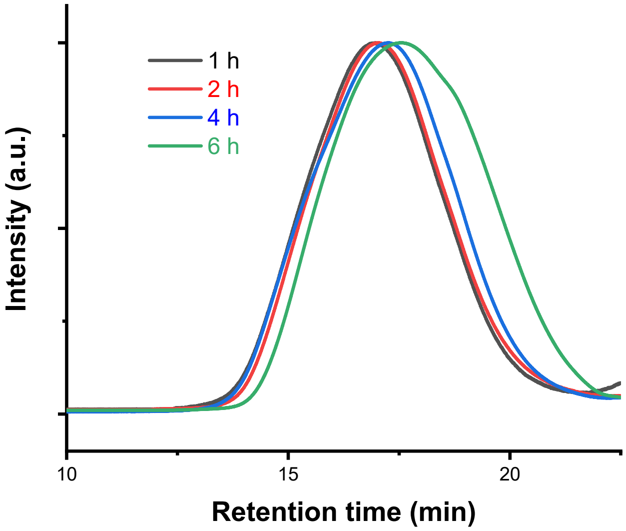

Figure S7. Size exclusion chromatogram of the polymers obtained in Entries 4-7.

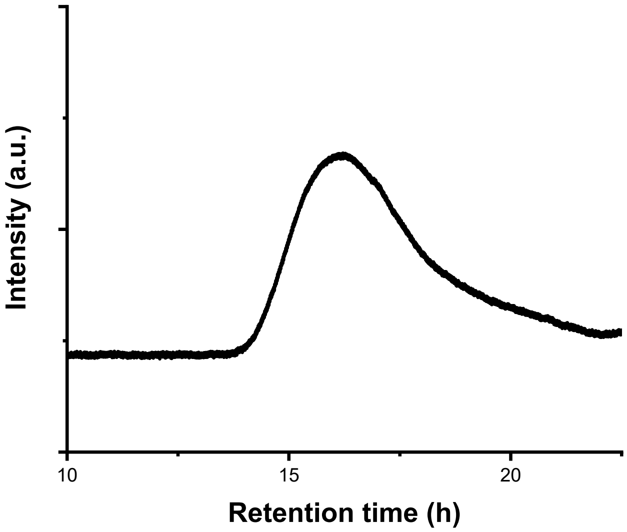

Figure S8. Size exclusion chromatogram of the polymer obtained in Entry 8.

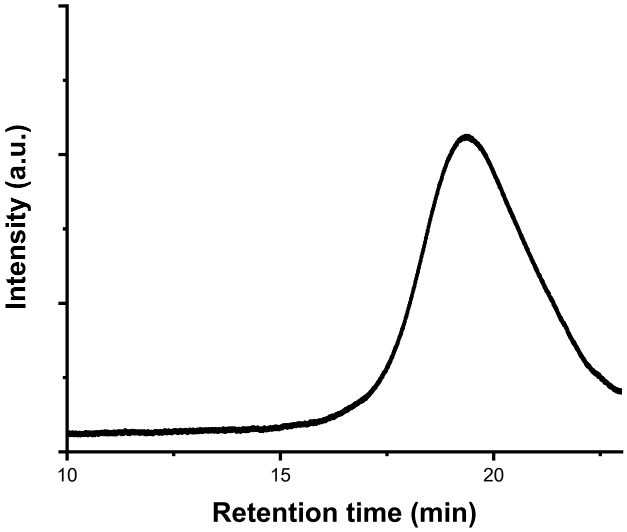

Figure S9. Size exclusion chromatogram of the polymer obtained in Entry 9.

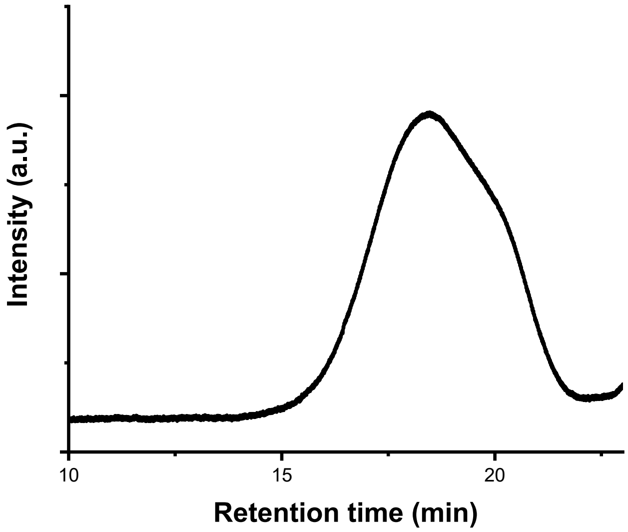

Figure S10. Size exclusion chromatogram of the polymer obtained in Entry 10.

6. Dynamic Light Scattering (DLS)

The size distributions of ZnO nanoparticles (ZnONPs) and water droplets in feed emulsion and filtrate were determined by the DLS technique on a Brookhaven DLS ZetaPALS instrument. ZnONPs were dispersed in 2-propanol with a concentration of 0.25 mM and feed emulsion was diluted 10 times for test. Data were collected using a 25 mW diode laser (λ=658 nm) at a fixed detector angle of 90º.

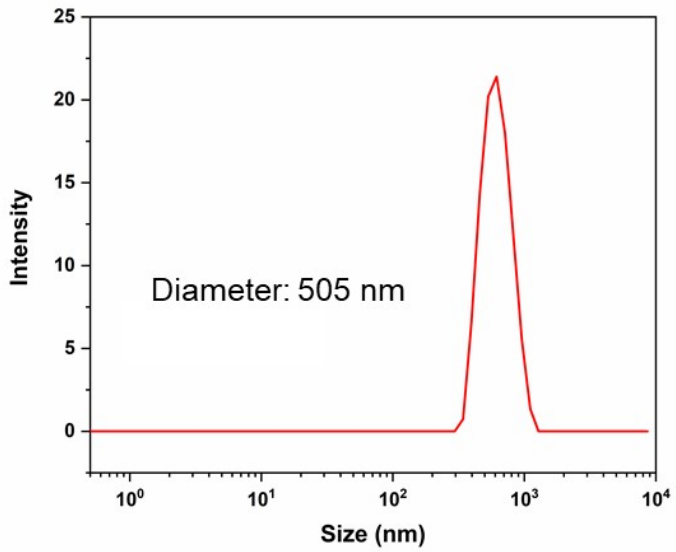

Figure S11. DLS data of ZnO nanoparticles

7. Mechanism Study

In order to confirm the radical initiation mechanism, EPR spectroscopy was conducted on a 1 wt% T-ZnO solution in IPA and a pure IPA as the control experiment. 10 mM DMPO was added to trap the short-lived radicals formed upon UV irradiation. The solution was injected into a 1 mm ID sample tube followed by 100 mW/cm^2 UV irradiation for 5 min before the spectrum was acquired. The hyperfine coupling constants *a* could be resolved from the difference in the field and the g factor was calculated according to the following equation with the microwave frequency ν and resonance magnetic field B : $g = \frac{71.4484 \times \nu(\text{GHz})}{B(\text{mT})}$

Table S1. EPR parameters for DMPO adducts of radicals

Parent radical	***g* factor**	***a*(N, NO) (G)**	***a*(H, C_2-H) (G)**
This work	2.0056	15.20	22.79
$C(OH)(CH_3)_2$[a]	2.0054	15.79	24.36

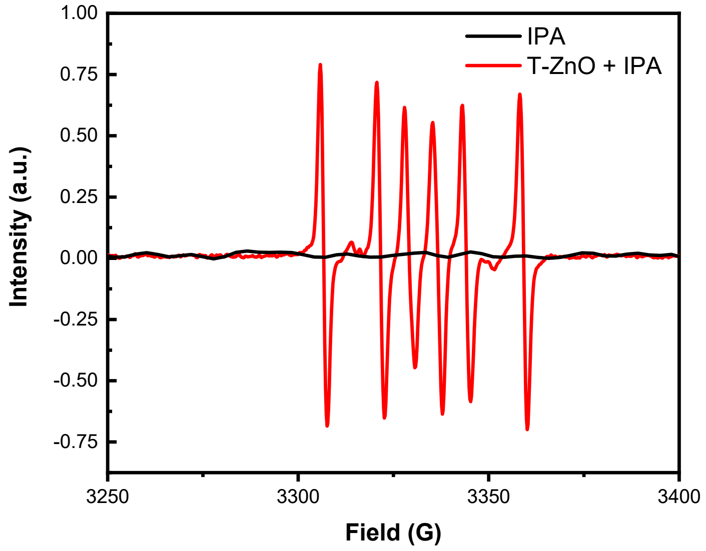

Figure S12. EPR spectra of the IPA solution with/without T-ZnO after UV irradiation.

[a] Data from literature.[3]

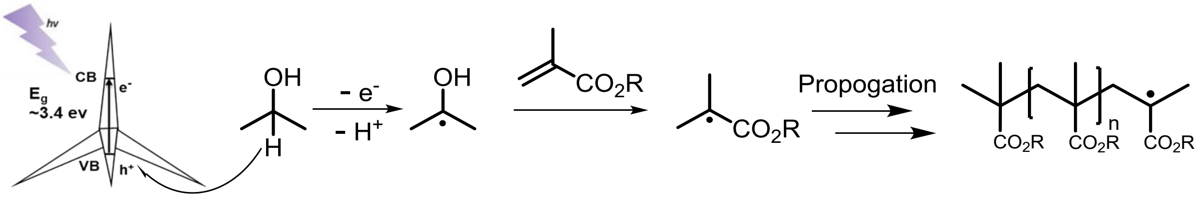

Figure S13. Proposed hole-mediated pathway of the T-ZnO initiated photopolymerization of methacrylate monomers.

The EPR experiment result confirmed the formation of neutral radical of IPA as a result of electron transfer to the hole of excited T-ZnO and proton loss. The radical initiation mechanism is proposed in Figure S10.

8. Static Water Contact Angles

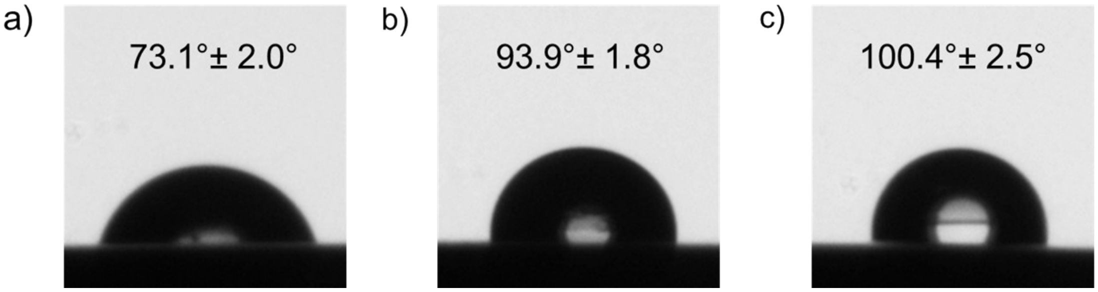

Figure S14. Images of water droplets on flat surfaces of (a) PMMA, (b) PBMA and (c) PLMA.

9. Scanning Electron Microscopy Images

Field-emission scanning electron microscopy (SEM) measurements were conducted on a JEOL JSM-7500F FE-SEM at 10 kV. Samples were taped on double side carbon tape and were coated with platinum/palladium for higher conductivity prior to tests.

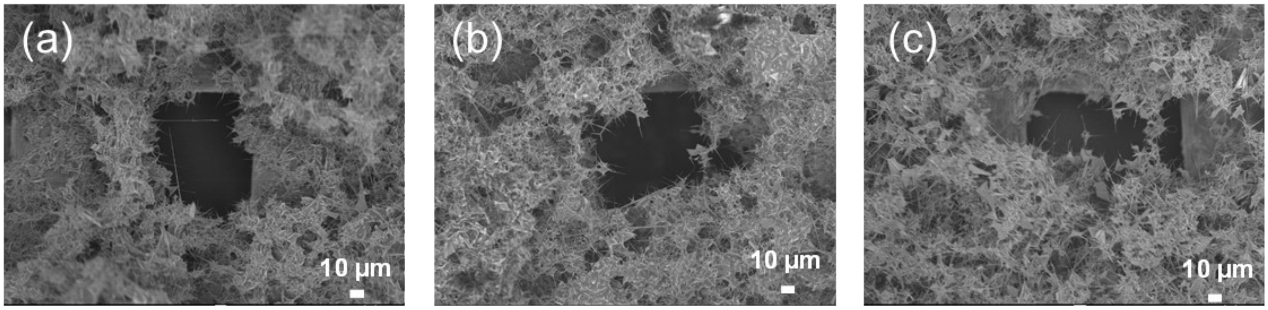

Figure S15. SEM images of (a) T-ZnO/PMMA-40; (b) T-ZnO/PBMA-40 and (c) T-ZnO/PLMA-40 coated stainless-steel mesh.

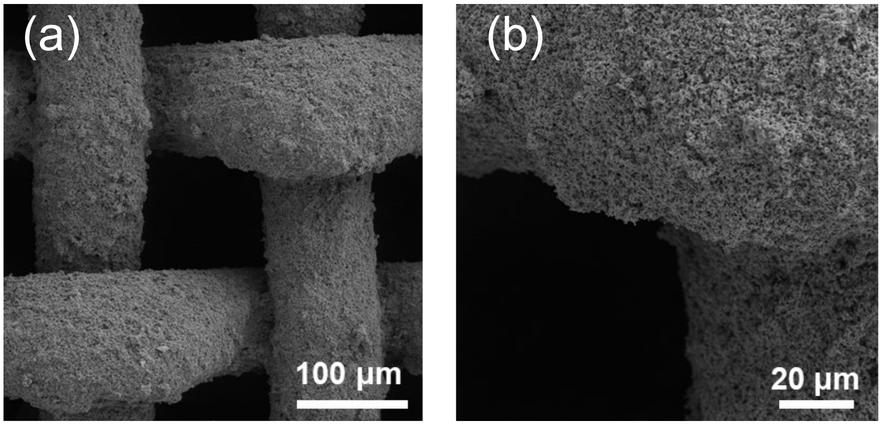

Figure S16. SEM images of ZnONP/PLMA-26 coated stainless-steel mesh

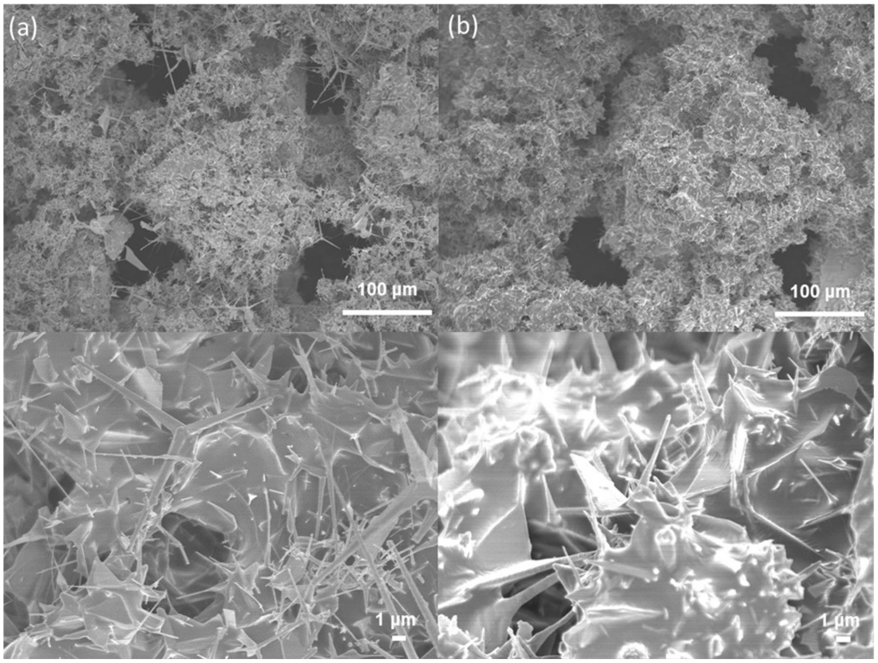

Figure S17. SEM images of T-ZnO/PLMA-40 coated stainless-steel mesh after (a) 600 water spray cycles and (b) 100,000 water droplets impact

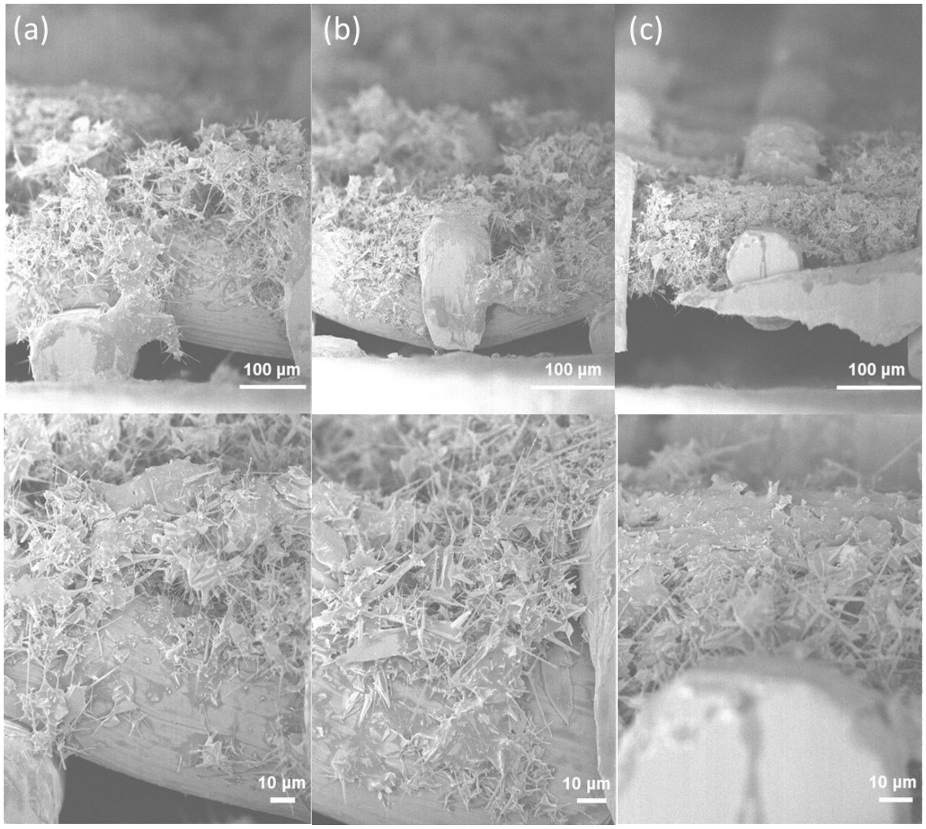

Figure S18. Cross-sectional SEM images of T-ZnO/PLMA-40 coated stainless-steel mesh: (a) before any mechanical impact; (b) after 600 water spray cycles; and (c) after 100,000 water droplets impact.

9. UV Influence on Surface Wettability

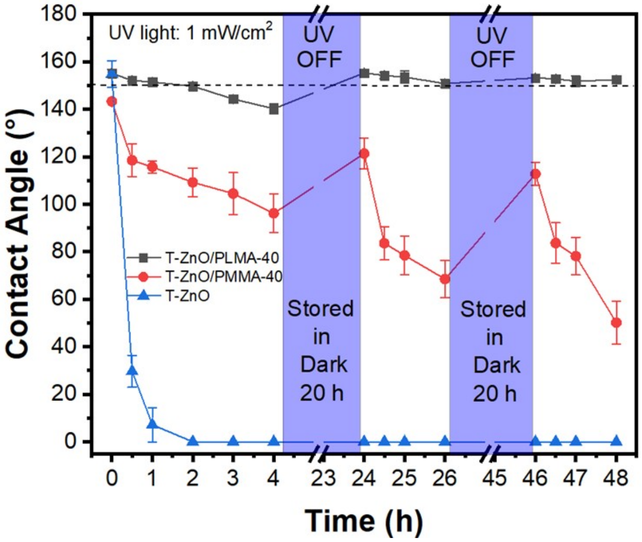

Figure S19. Changes in static contact angles of T-ZnO/PLMA-40, T-ZnO/PMMA-40 and T-ZnO control samples on UV irradiation.

10. References

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3. H. Taniguchi and K. P. Madden, *Radiation Research*, 2000, **153**, 447-453, 447.