Electronic Supplementary Material (ESI) for Materials Horizons.

Slippery hydrogel surface on PTFE hollow fiber membranes for sustainable emulsion separation

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Electronic Supplementary Information

Experimental Section.

Materials.

Commercial PTFE hollow fiber membrane (average pore size: 0.1 μm, outside diameter: 2 mm, inside diameter: 1 mm) was obtained from Water Art Membrane Technology Development Co., Ltd. (Ningbo, China). Sulfuric acid (H_2SO_4, AR, 95%-98%), Triethyl phosphate (TEP, CP), vinyltriethoxysilane (VTES, CP) were acquired from Sinopharm Chemical Reagent (Shanghai) Co., Ltd. Dimethoxydimethylsilane (DMS, 97%), 2,2-Azodiisobutyronitrile (AIBN, 98%), n-vinylpyrrolidone (NVP, 99%, containing 100 ppm NaOH stabilizer), Decamethylcyclopentasiloxane (D5, GC, ≥99.0%), Nile red were got from Aladdin Reagent (Shanghai) Co., Ltd. Hexadecane (AR, 98%), citric acid (98%), n-hexane (AR, 97%), isooctane (AR) were purchased from Shanghai McLean Biochemical Technology Co., Ltd.

Preparation of PVP-VTES hydrophilic modifier.

The synthesis method of hydrophilic modifiers refers to previous work.[33] Especially, 15.0 g of NVP, 11.0 g of VTES and 0.4 g of AIBN were then dissolved in 400.0 g of TEP at ambient temperature and heated to 80 °C under an N_2 atmosphere. After reacting for 12 h, PVP-VTES hydrophilic modifier was produced.

Preparation of PTFE-PVP hollow fiber membrane.

Firstly, the pristine PTFE hollow fiber membrane was immersed in ethanol with oscillation for 5 h to completely saturate the membrane. The PVP-VTES hydrophilic modifier was then mixed with water in a 1:1 (v/v) ratio. Subsequently, wet PTFE membrane was submerged into the above modifier for 4 h, followed by crosslinked at 60°C for 18 h in 2 wt% citric acid aqueous solution. The resulting PTFE-PVP hollow fiber membrane was laundered with water to exclude residual polymers and then dried at room temperature.

Preparation of PTFE-PVP-PDMS hollow fiber membrane.

PTFE-PVP hollow membrane was infiltrated with water and encapsulated in the inner lumen. Afterwards, the membrane was immersed in a 1 wt% H_2SO_4 aqueous solution for 1 min and 4 wt% DMS-hexane solution for 1 min, respectively. Lastly, the reaction

was carried out at 21 °C with 55% humidity for 5-25 min. The as-prepared membrane was named as PTFE-PVP-PDMS hollow fiber membrane.

Characterizations.

Microstructure and elemental distribution of membrane was visualized by Field emission SEM (Hitachi-S4800, Japan) and TEM (Themo-Fisher, Talos-F200x, USA). As for TEM, the thickness of the PDMS layer on the outer surface of the PTFE-PVP-PDMS hollow fiber membrane was scanned. For the surface chemistry of the resultant membranes, Micro-FTIR (Agilent, Cary 660-620, USA) and XPS (Kratos, Axis-Supra, Britain) were employed for characterization. Thermogravimetric analysis (TG, 209F1) was performed under a nitrogen atmosphere (purge at 20 mL/min). Thin sample were heated from room temperature to 800°C at 10 °C/min. TOF-SIMS (5-100 IONTOF GmbH, Germany) was applied to investigate the spatial profiling of surface atoms on PTFE-PVP-PDMS hollow fiber membrane. Depth profiles of F^-, SiO^{2-}, SiO^{3-}, and $SiHO^{3-}$ were obtained with Cs^+ cluster ions (60 nA, 300 μm × 300 μm) as sputter species and Bi^{3+} (0.75 pA, 100 μm × 100 μm) as ion species. Dynamic WCA and UOCA was measured by OCA25 Tester (Dataphysics, Germany). Membrane pore size was determined by gas-liquid through-hole aperture analyzer (BSD-PB, China). Distribution and content of oil droplets in the feed and filtrate was studied by optical microscopy (Olympus-BX51, Japan), DLS (Zetasizer-Nano ZS, Malvern, UK), TOC (Multi N/C-3100, Analytikjena, Germany). SPM (Dimension-icon, Bruker, USA) was applied to test the adhesion force of membrane surface to oil. Optical microscope (Olympus-BX51, Japan) was used to verify the movement of oil phase in emulsion on the surface of hollow fiber membrane. Biological Laser Confocal Microscope (LEICA, TCS SP5) was used to observe the distribution of the oil phase on the membrane surface before and after emulsion separation. The oil phase in the lotion is dyed by Nile red.

Separation performance of oil-in-water emulsion.

Membrane separation and long-term antifouling of oil-in-water emulsions were assessed by a home-made cross flow filtration apparatus. Here, one end of the membrane filament is closed and one end is open. The open end is fixed in the separation device as the outlet, and the closed end is placed in the device in a free form

(Figure S2). The membrane module consists of four 10 cm hollow fibers with an effective separation area of 25.4 cm². Due to the soft texture of the PTFE membrane filament, a copper wire with a diameter of 5 mm is placed inside the membrane cavity as a support. With the peristaltic pump providing the driving force and the staggered flow shear force, the copper wire will vibrate with the oscillation of the water flow. This cross flow mode operates at a pressure of 10 kPa with a time interval of 20 min between filtrate collections. The permeability ($P_{cross\ flow}$) was estimated based on Eq. 1.

$$P_{cross\ flow} = \frac{\Delta V}{A_{eff} t} \quad (1)$$

Where ΔV (L) is the volume of filtrate collected at the time interval t (h). A_{eff}(m²) is the effective separation area of the membrane filament.

The separation efficiency (S_e)was estimated based on Eq. 2.

$$S_e = \frac{E_{oil} - F_{oil}}{E_{oil}} \times 100\% \quad (2)$$

Where E_{oil} and F_{oil} is the are the oil content in the emulsion and filtrate, respectively.

Wherein, the oil-in-water emulsion was formed by mixing 0.2 g of SLS, 20 mL of oil (D5, hexadecane, cetane and iso-octane) and 2000 mL of water at 800 rpm for 6 h.

The movement state of emulsion on the membrane surface.

The hollow fiber membrane was dissected along the central axis and the dissected surface was fixed on a slide. Then focus the hollow fiber membrane in the light microscope and turn the video on. Finally, drop the emulsion and observe the movement of the emulsion on the surface of the membrane.

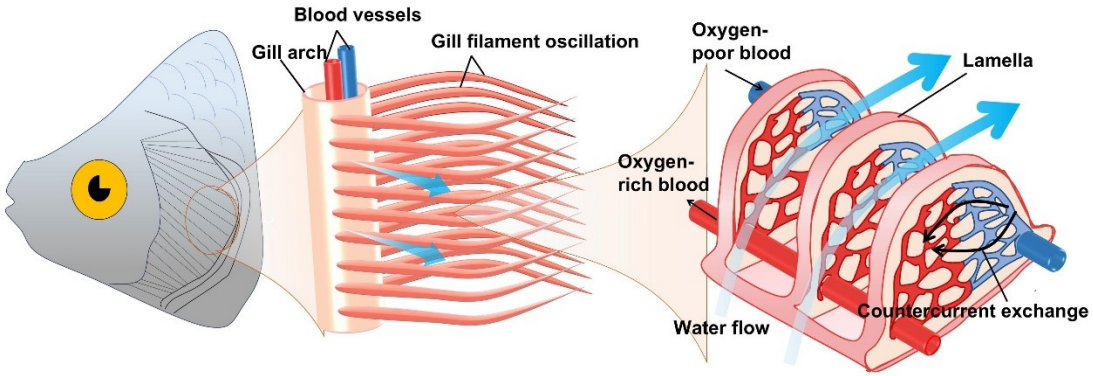

Figure S1. Schematic diagram of the working principle of gill respiration and dynamic anti fouling in fish.

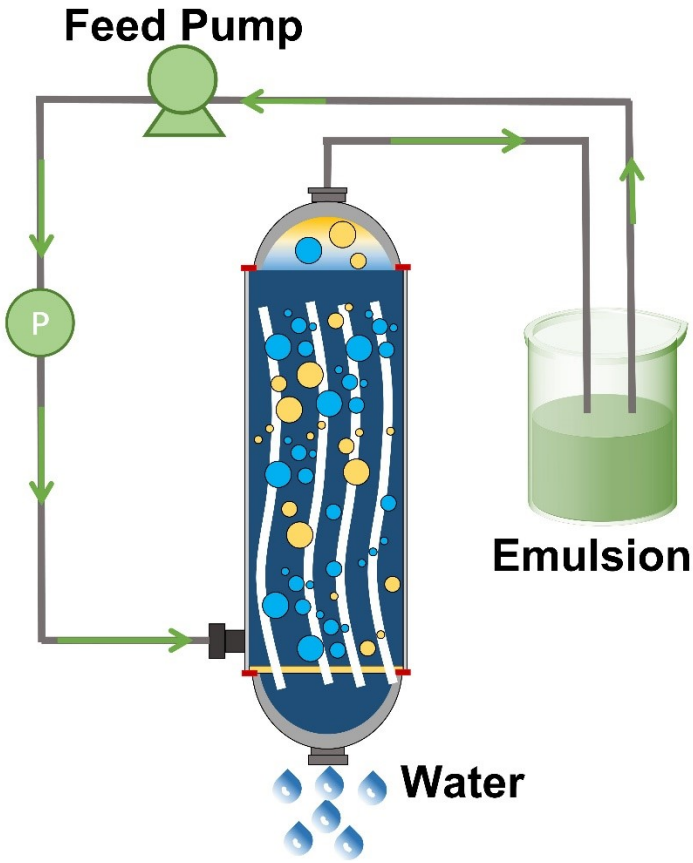

Figure S2. Home-made crossflow device for oil-in-water emulsion separation.

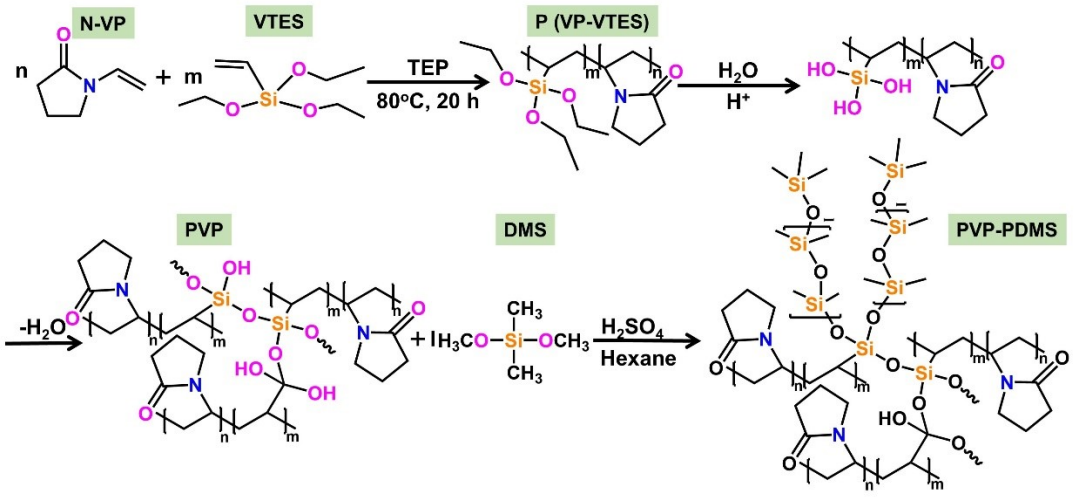

Figure S3. Schematic diagram of the stepwise modification mechanism of heterogeneous PTFE-PVP-PDMS hollow fiber membranes.

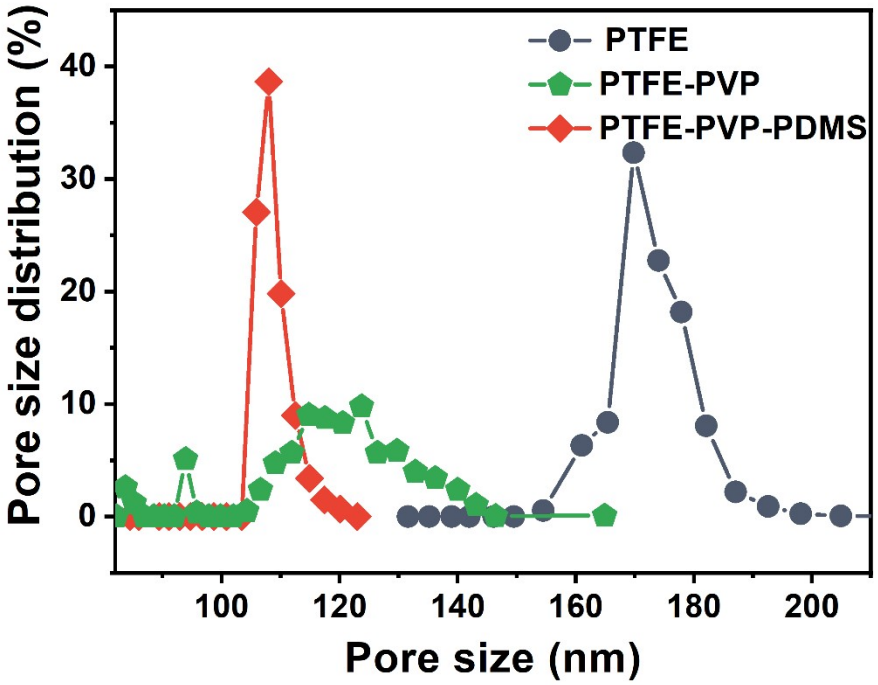

Figure S4. Pore size distribution of PTFE, PTFE-PVP, PTFE-PVP-PDMS membranes.

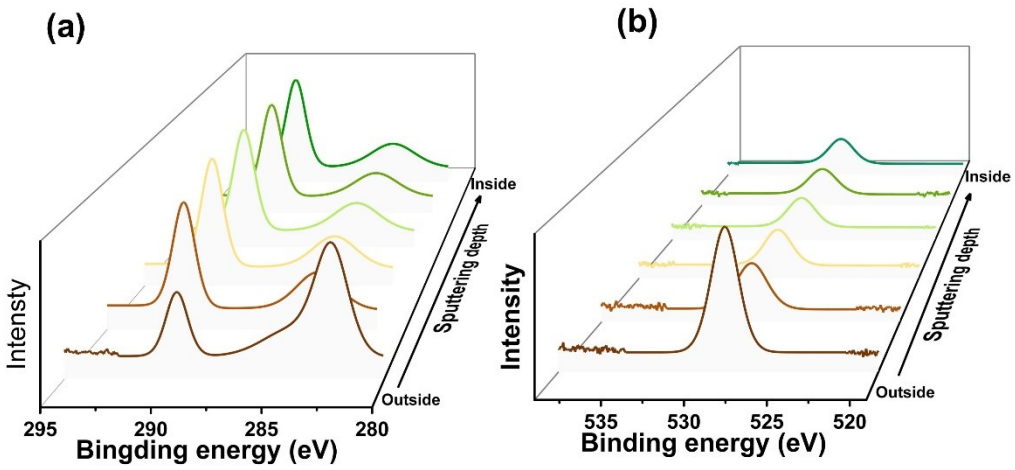

Figure S5. Dynamic depth profiles of XPS. (a) The peak intensity of C and O elements varies with sputtering depth for PTFE-PVP-PDMS membrane.

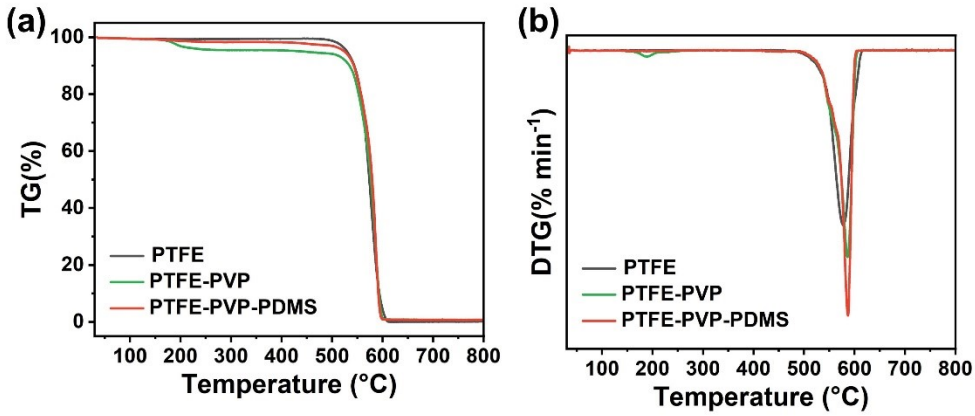

Figure S6. (a) TG and (b) DTG curves of PTFE, PTFE-PVP, PTFE-PVP-PDMS membrane.

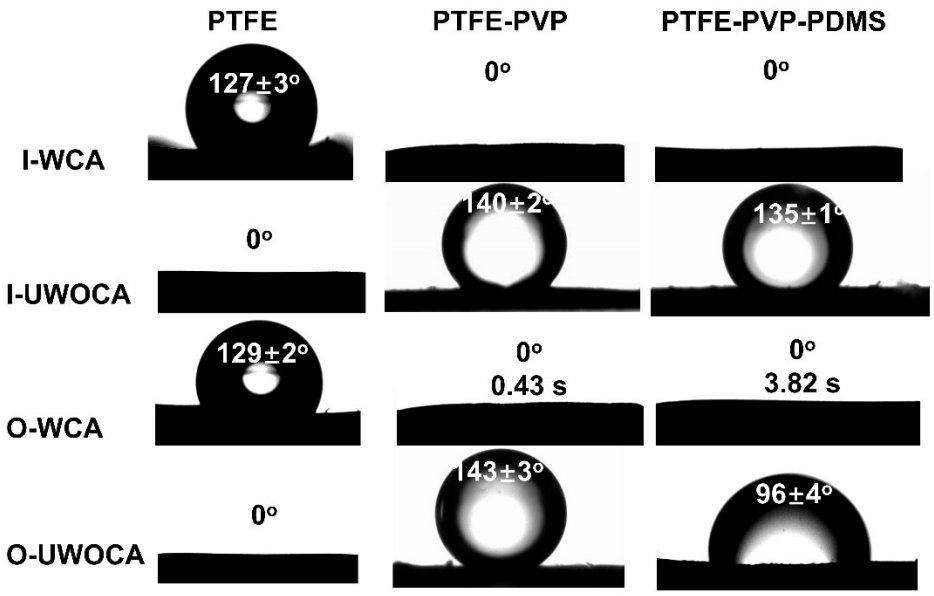

Figure S7. The wettability of water and underwater oil on the inner and outer surfaces of PTFE, PTFE-PVP, and PTFE-PVP-PDMS hollow fiber membranes.

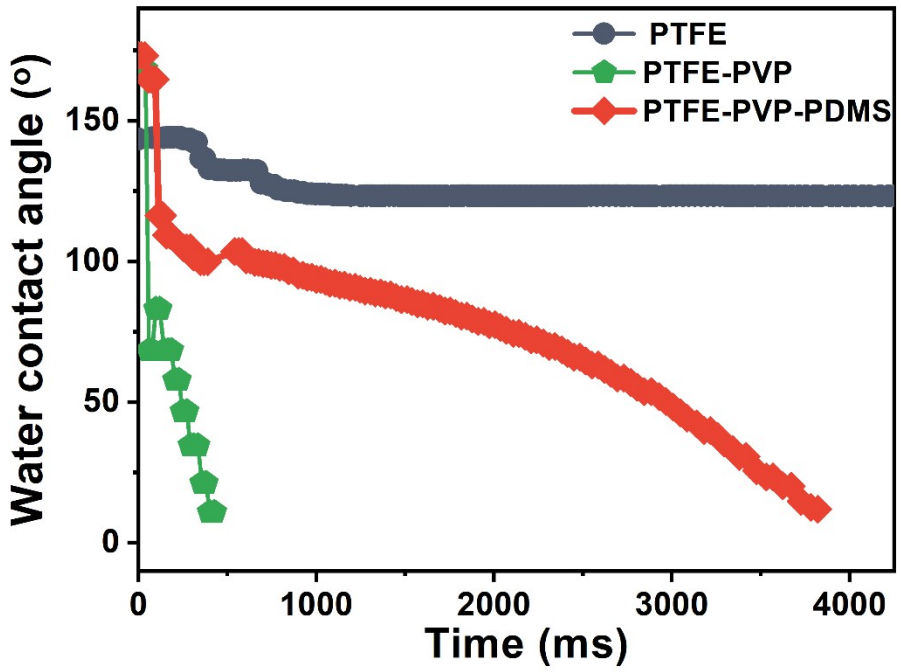

Figure S8. The relationship between water wettability in air on the outer surface of PTFE, PTFE-PVP, PTFE-PVP-PDMS hollow fiber membranes and time.

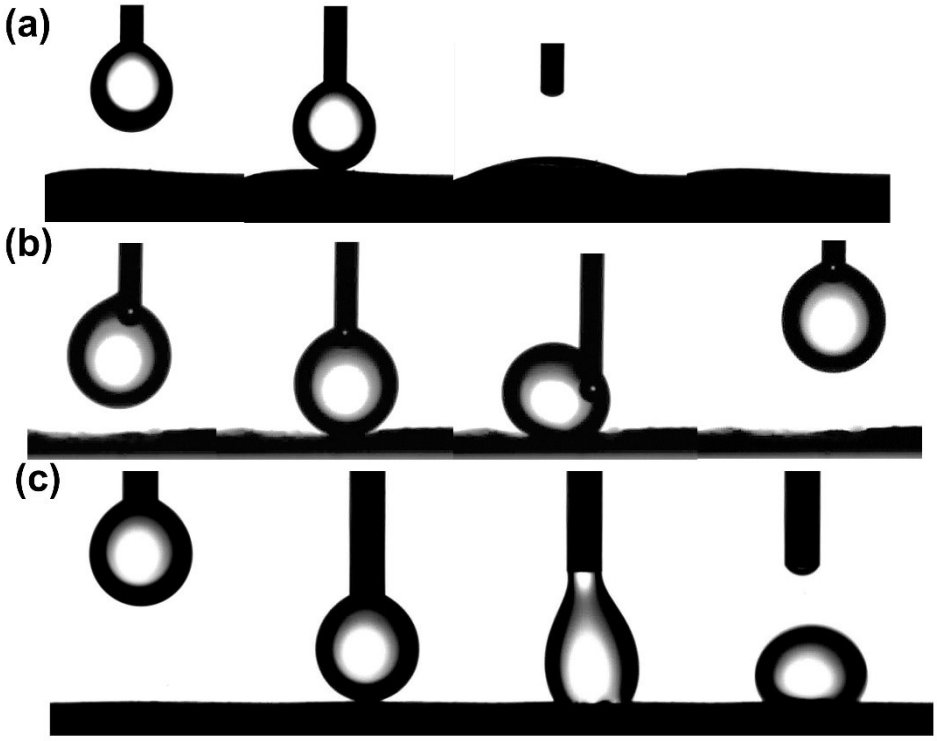

Figure S9. Oil adhesion resistance under water of (a) PTFE, (b) PTFE-PVP, (c) PTFE-PVP-PDMS membrane.

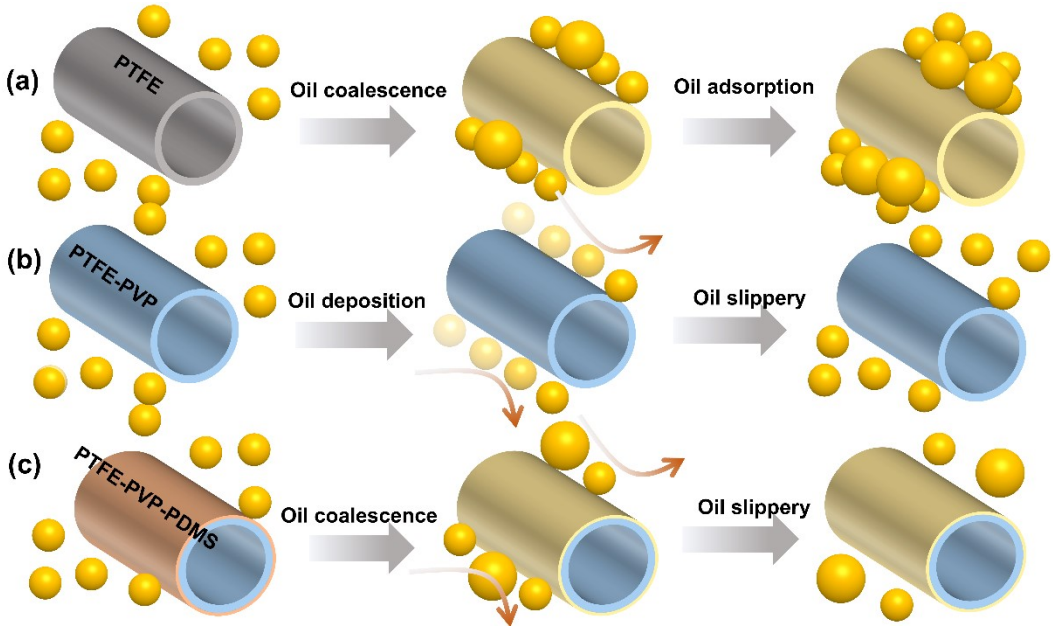

Figure S10. The movement of oil droplets on the surface of the (a) PTFE, (b) PTFE-PVP, (c) PTFE-PVP-PDMS membrane in emulsion.

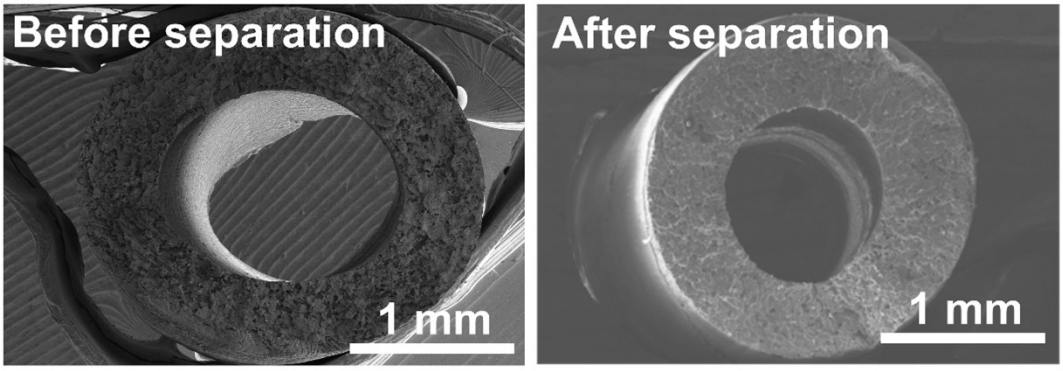

Figure S11. The morphology of the membrane before and after separation under a pressure of 10 Kpa.

There is no significant change in the morphology after separation compared to before separation.

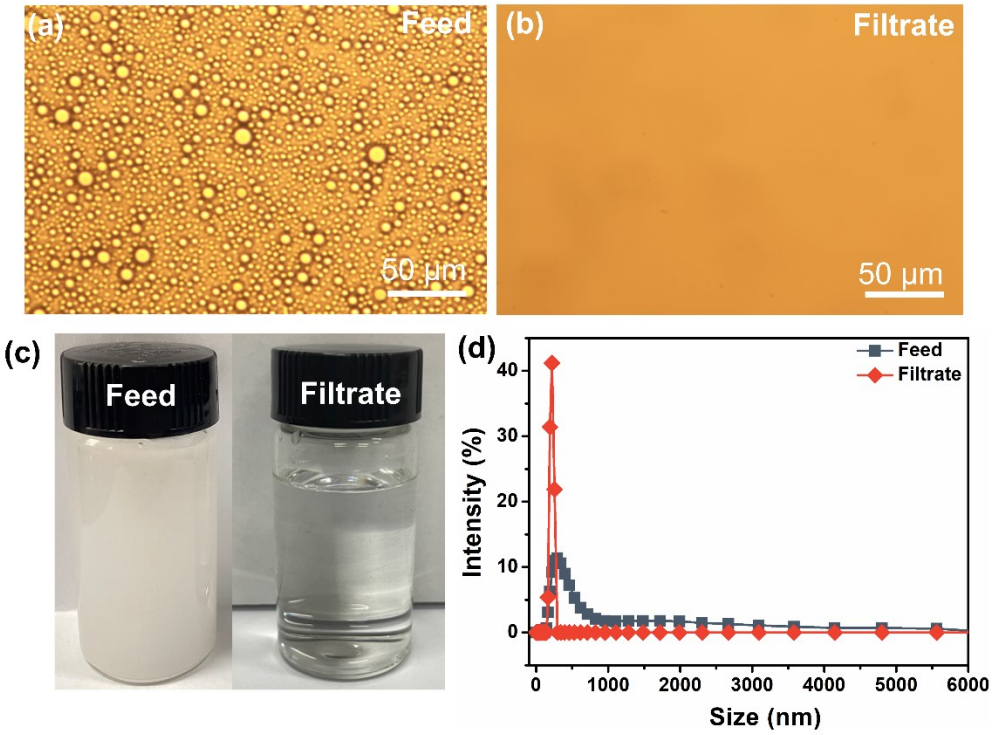

Figure S12. Emulsion changes before and after separation. (a-b) Optical microscopy of emulsions, (c) Macrophotographs and (d) particle size distributions before and after separation.

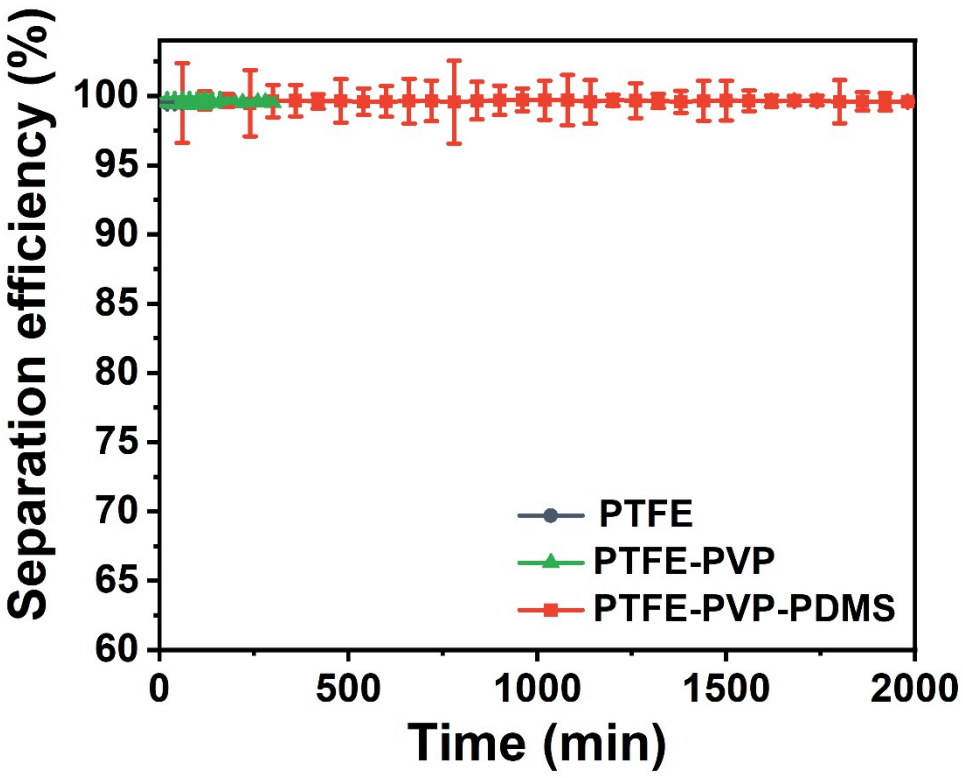

Figure S13. The separation efficiency of PTFE, PTFE-PVP and PTFE-PVP-PDMS membrane for D5-in-water emulsion.

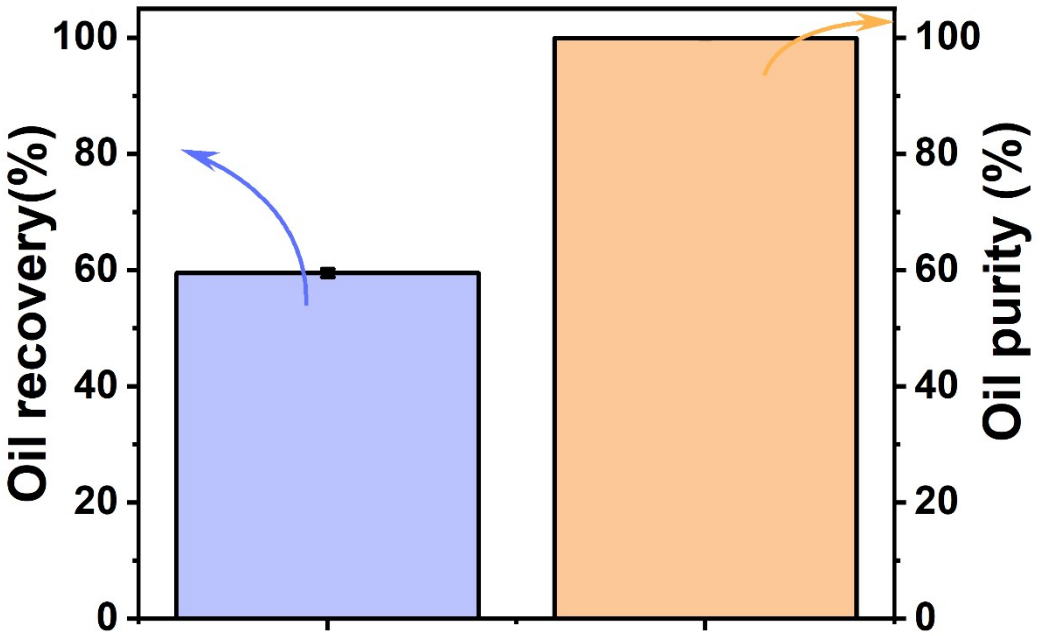

Figure S14. Oil recovery and oil purity of PTFE-PVP-PDMS membranes after separating D5-in-water emulsion for 2000 min.

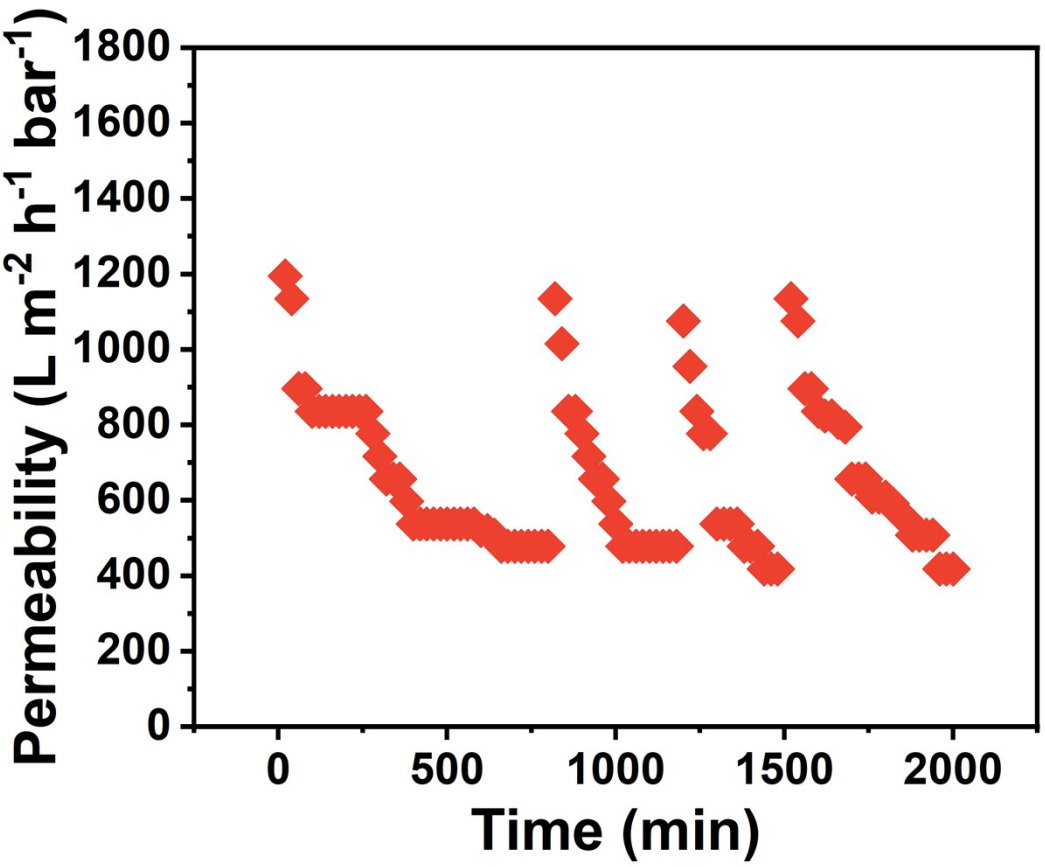

Figure S15. Permeability recovery of PTFE-PVP-PDMS membranes in a four-cycle "ethanol wash" operation.

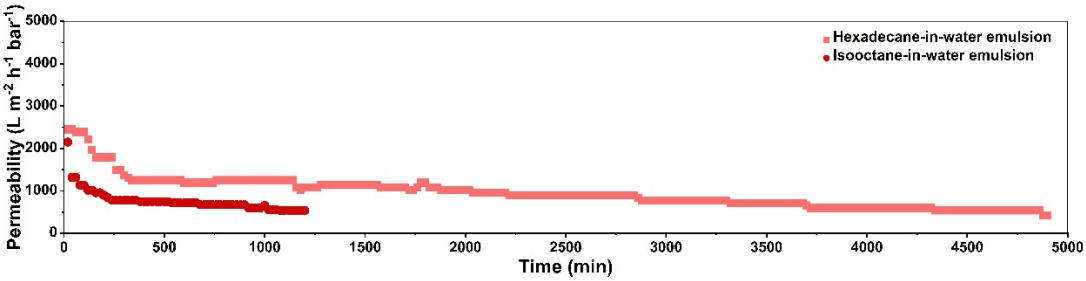

Figure S16. Real-time water permeability variation of PTFE-PVP-PDMS membrane for hexadecane and isooctane-in-water emulsion.

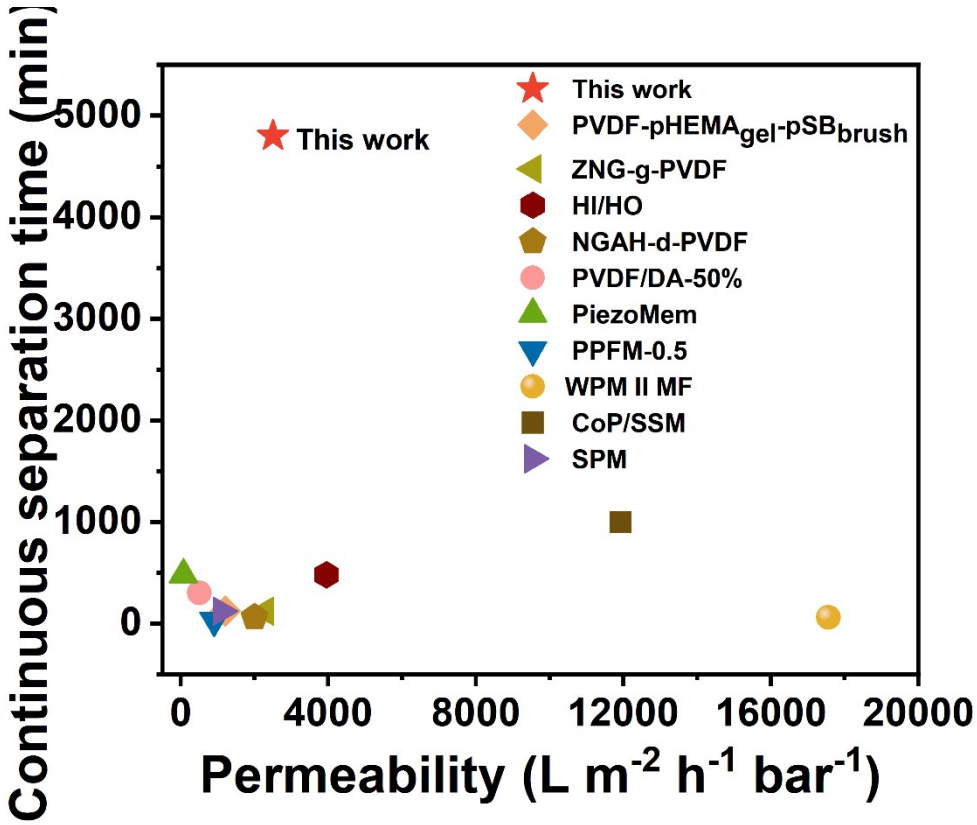

Figure S17. Relationship between permeability and separation time for different work.

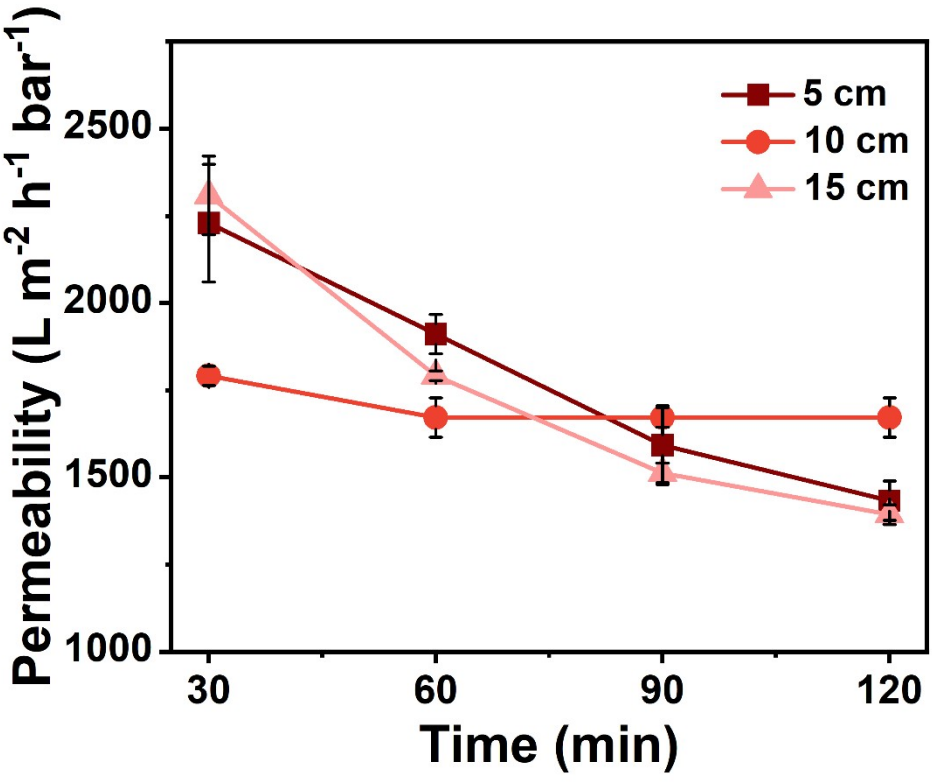

Figure S18. The influence of membrane filament length on separation stability.

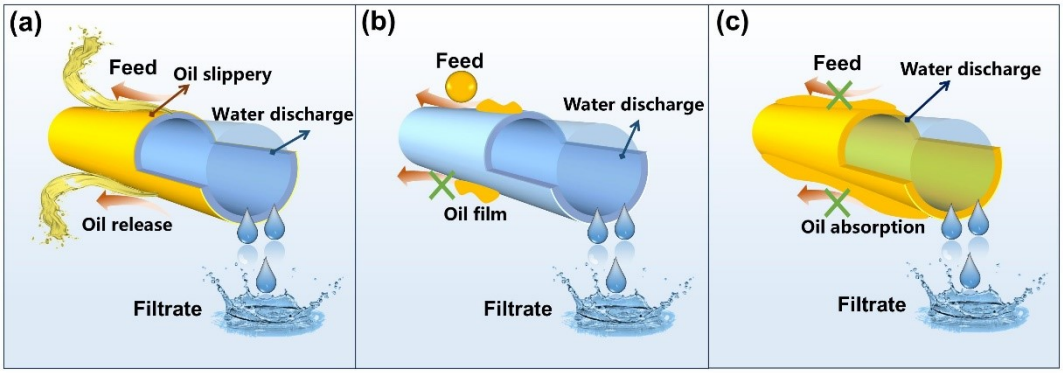

Figure S19. Schematic representation of the behavior of oil droplets when they contact the surface of PTFE-PVP-PDMS, PTFE-PVP, PTFE and membranes, respectively.

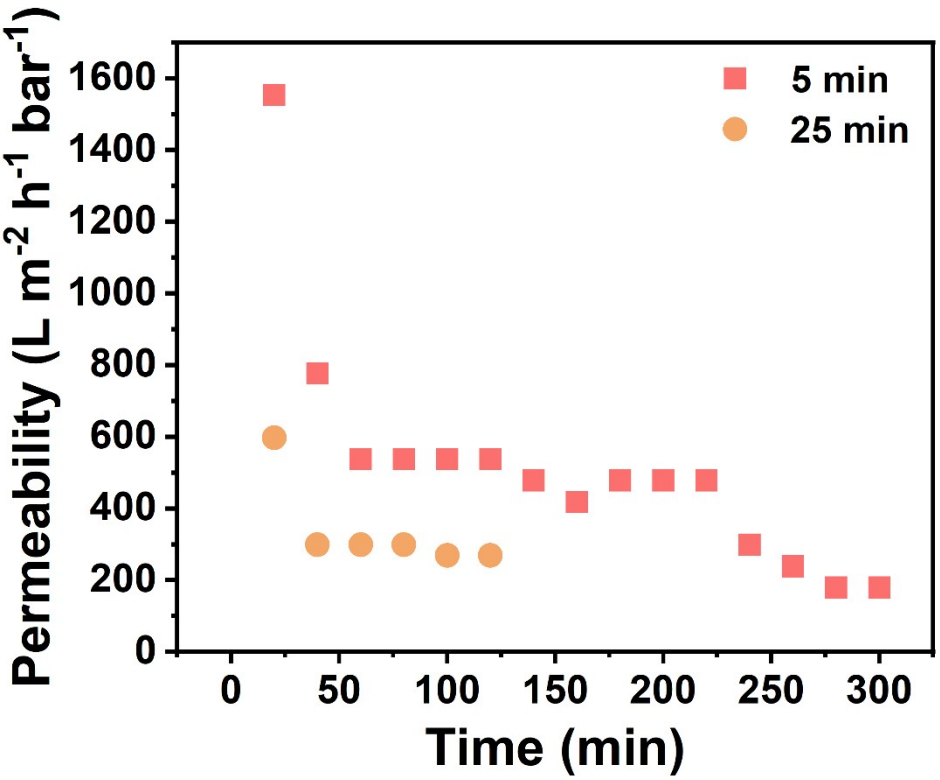

Figure S20. Real-time water permeability variation of PTFE-PVP-PDMS membranes with different modification times.

Video S1: Oil droplet contact–depart on the surface of PTFE membrane.
Video S2: Oil droplet contact–depart on the surface of PTFE-PVP-PDMS membrane.
Video S3: Oil droplet contact–depart on the surface of PTFE-PVP membrane.
Video S4: Movement of oil droplets in emulsion on the surface of PTFE membrane under optical microscope.
Video S5: Movement of oil droplets in emulsion on the surface of PTFE-PVP membrane under optical microscope.
Video S6: Movement of oil droplets in emulsion on the surface of PTFE-PVP-PDMS membrane under optical microscope.