Supporting Information

Bead-like Porous Fibrous Membrane with Switchable Wettability for Efficient Oil/Water Separation

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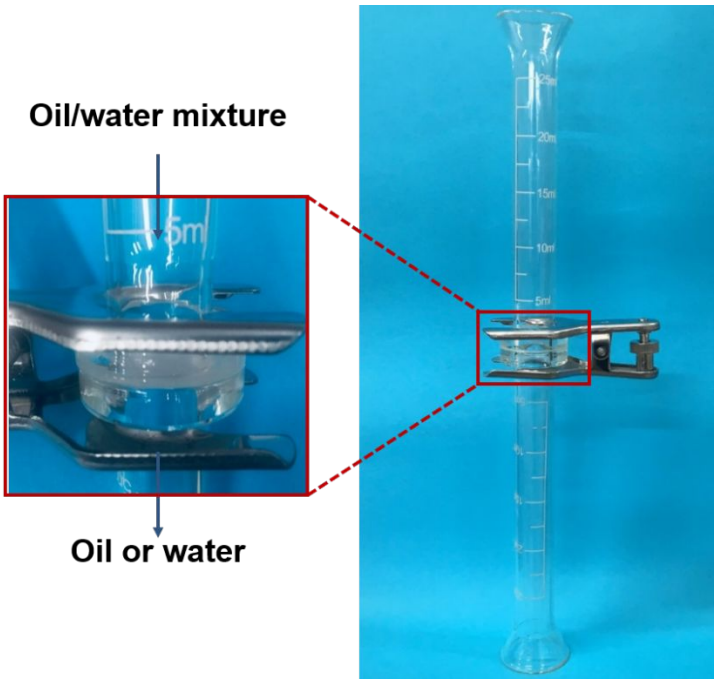

Figure S1 The digital photograph of gravity-driven separation device.

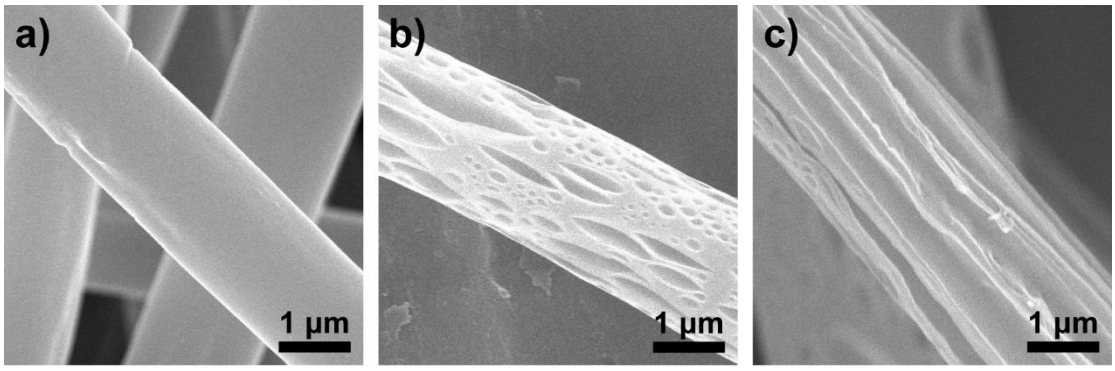

Figure S2 (a-c) SEM images of the PS fibers fabricated from solutions with solvent composition of D0T-3, D20-3, and D40-3, respectively.

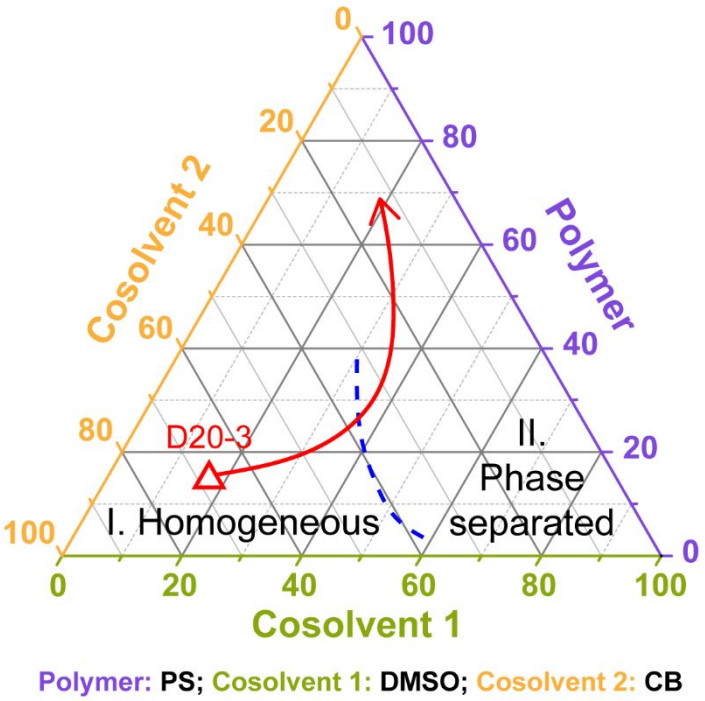

Figure S3 Phase diagram of the PS/CB/DMSO ternary system based on weight fraction at room temperature.

PS fibrous membranes spun with solutions of different solvent composition were denoted with D0T-3, D20-3, and D40-3, respectively. The cosolvent is composed of a good solvent (CB) and a nonsolvent (DMSO), and the evaporation rate of CB is higher than that of DMSO. When the content of DMSO is zero, PS molecular chains migrate to the outside forming the shell during the rapid evaporation of CB (Figure S2a). As the proportion of DMSO increases, phase separation occurs after the solution passing through the liquid-liquid demixing line (Figure S3). As shown in Figure S2b, the polymer-rich phase forms the fiber body, while the solvent-rich phase forms the pore during the drying progress. For D40-3, the pores are further enlarged, leading to the formation of gully-shaped structure on the fiber surface.

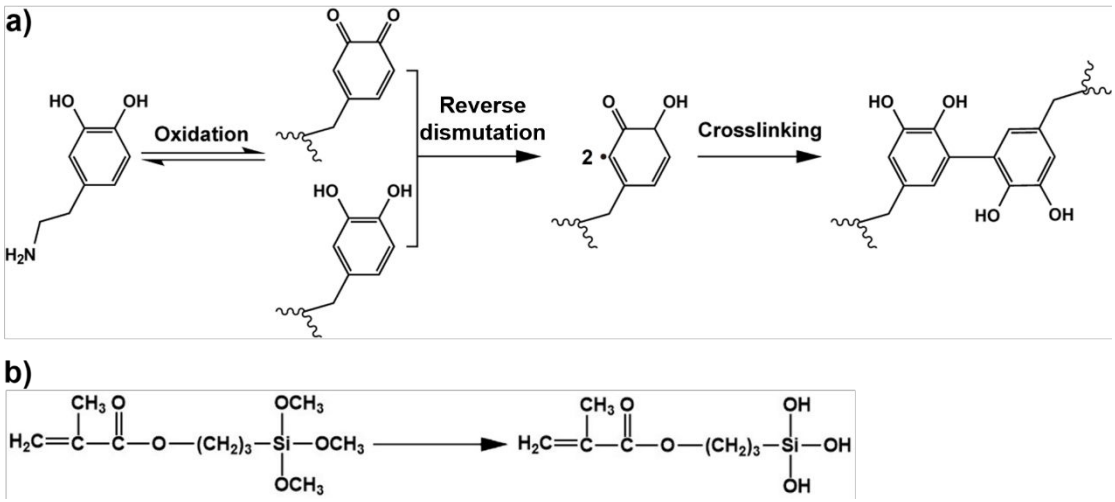

Figure S4 The reaction routes involved in pretreatment progress, (a) the auto-polymerization reaction of dopamine and (b) the alcoholysis reaction of KH570.

The catechol and amino groups of dopamine are similar to an adhesion protein of the mussels that closely adheres to the surface [S1]. A kind of adhesion mechanism of dopamine is proposed in Figure S4a. In the weak base solution, the catechol groups on dopamine are easily oxidized to the ortho-benzoquinone structure; a reverse dismutation reaction occurs between dopamine and dopaquinone to form the semiquinone radical, which is coupled to form the polydopamine (PDA) layer and adheres tightly to the surface of the matrix material [S2]. As shown in Figure S4b, the methoxy groups on KH570 are susceptible to alcoholysis, and the silanol groups could undergo dehydration condensation reaction with a large amount of hydroxyl groups on the surface of the PDA-treated porous PS fibrous membrane.

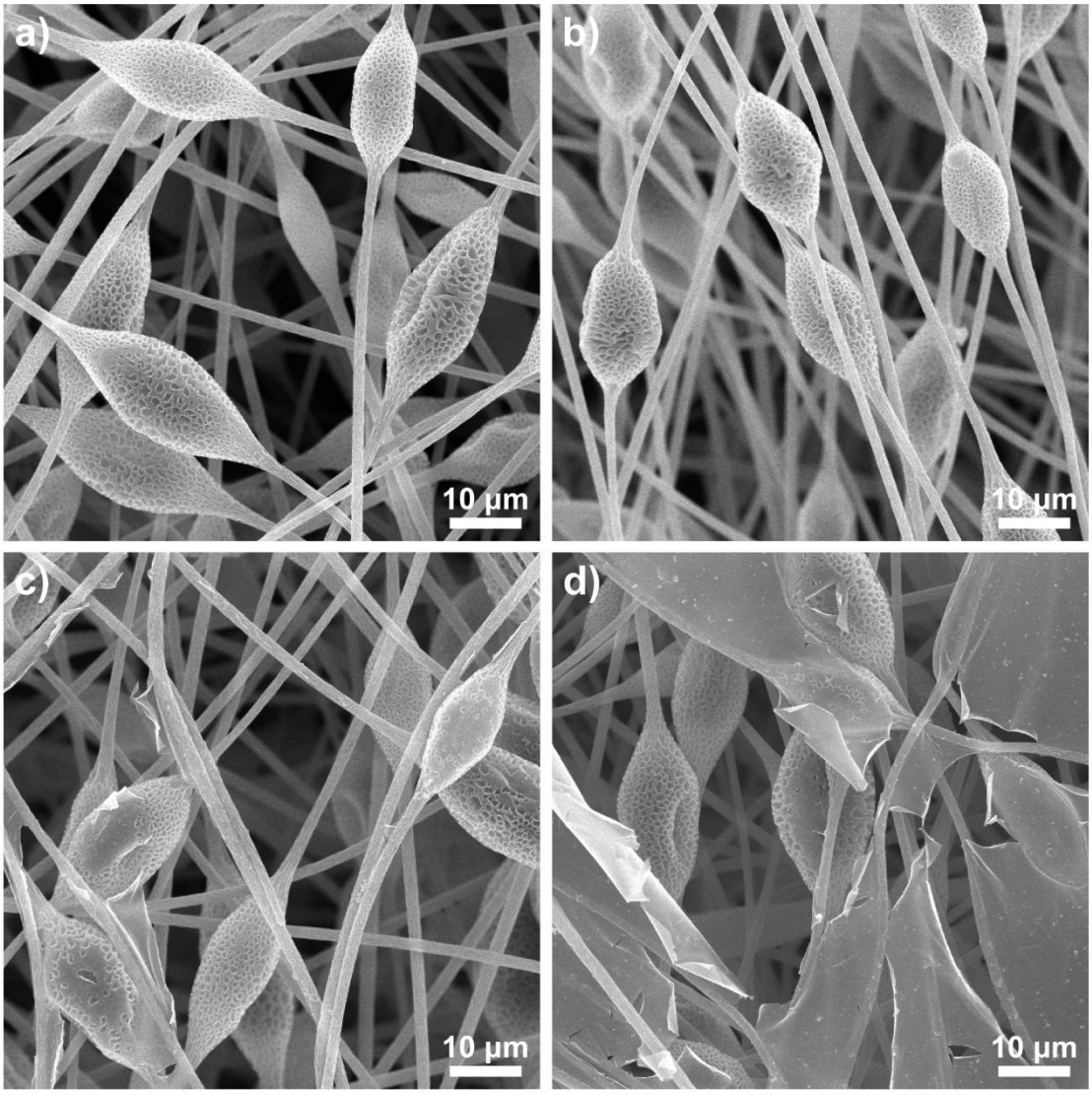

Figure S5 (a-d) SEM images of the PS fibrous membranes treated with dopamine solutions of 0.1, 1, 2 and 6 mg mL^{-1} for 2 h at ambient temperature, respectively.

As the concentration of the dopamine solution increases, the surface of the porous PS fibrous membrane is gradually covered by the PDA layer after treated in the same time (2 h). For the dopamine solutions of 2 and 6 mg mL^{-1}, the pore structure on the fibers and beads is filled with PDA, which will reduce the roughness of the porous PS fibrous membrane. In addition, the PDA layer is rich in hydroxyl groups, resulting in the decline in the hydrophobicity of membrane.

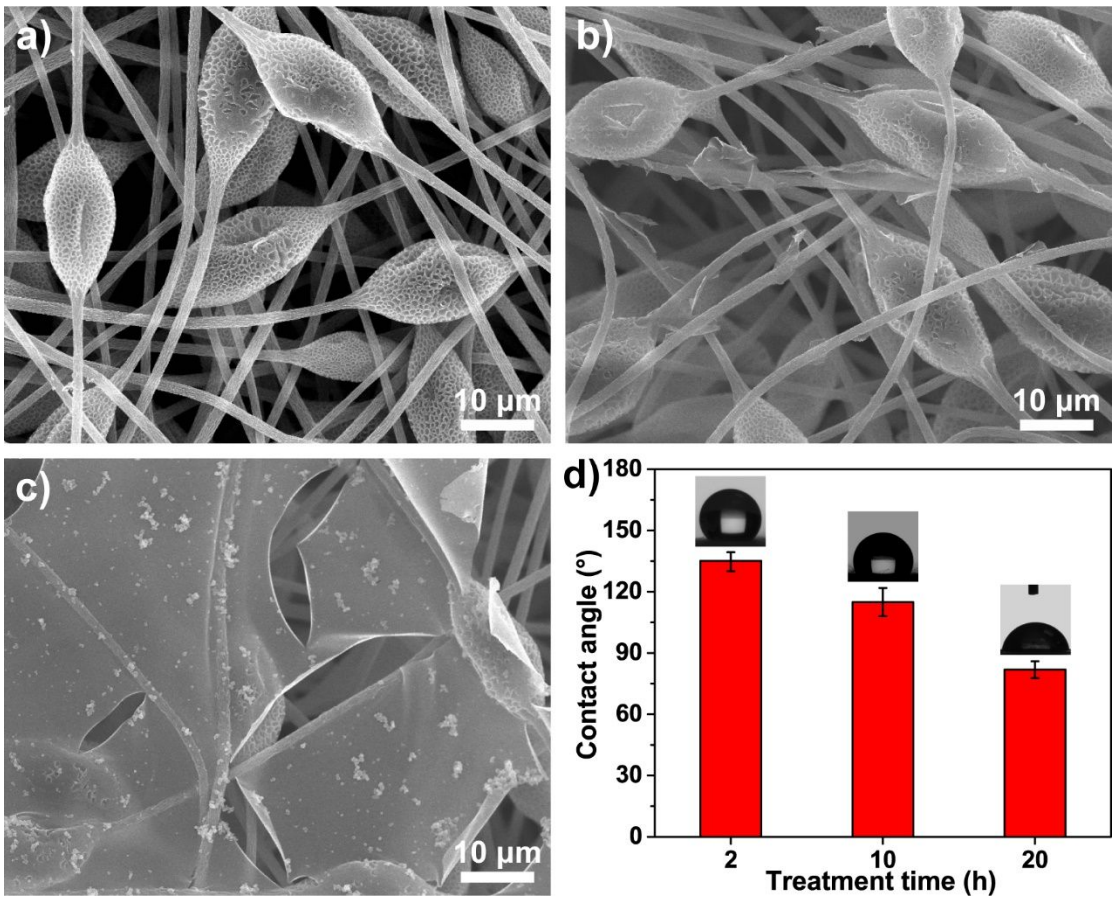

Figure S6 (a-c) SEM images of the PS fibrous membranes treated with 1 mg mL^{-1} dopamine solutions for 2, 10 and 24 h, respectively. (d) Contact angle plots of the PS fibrous membranes treated with 1 mg mL^{-1} dopamine solutions in different treatment time.

The treatment time also has great impact on the morphology and wettability of the porous PS fibrous membrane. In Figure S6, as the treatment time extends from 1 h to 24 h, the PDA layer appears gradually, and eventually covers the surface of the membrane. Similarly, the hydrophobicity of the membrane is weakened owing to the loss of pore structure and the introduction of hydroxyl groups. The value of contact angle changes from 130.1° to 81.2°, and the surface wettability transforms from hydrophobic to hydrophilic.

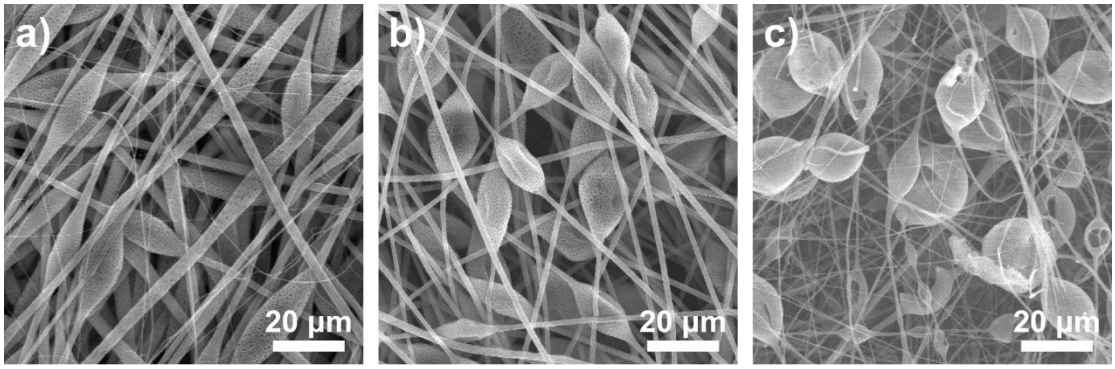

Figure S7 (a-c) SEM images of the PS fibrous membranes under electrospinning feed speed of 0.25, 0.5, and 1.0 mL h^{-1}, respectively.

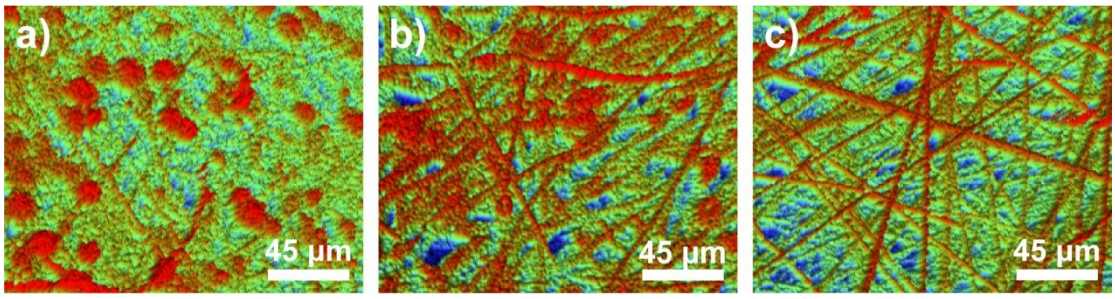

Figure S8 The R_a values of the PS fibrous membranes with different concentrations (100, 200, and 300 mg mL^{-1}).

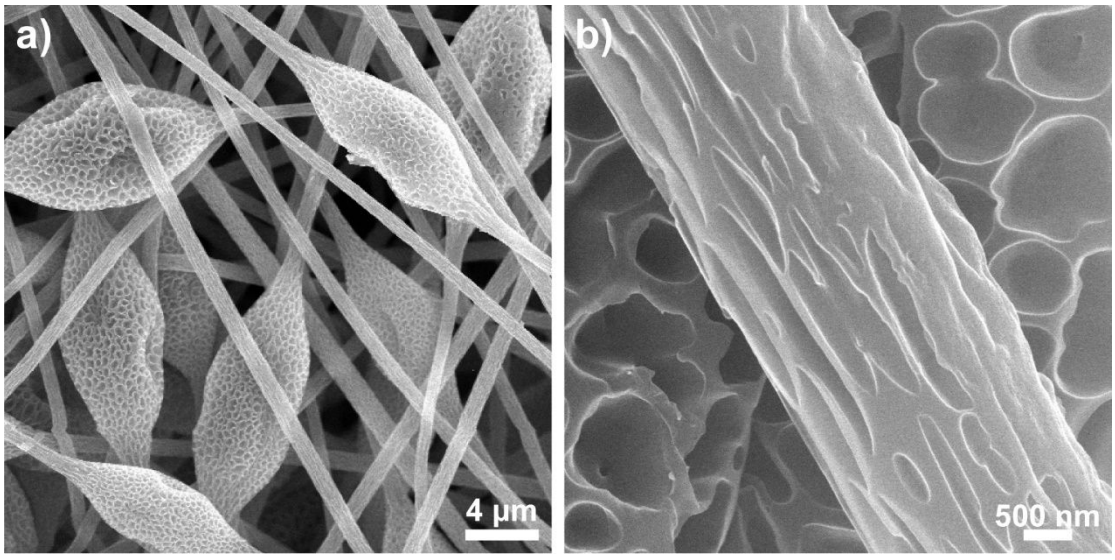

Figure S9 (a and b) SEM images of $PDMEMA_4$-$PTFOA_1$/PS.

As shown in Figure S9a, $PDMEMA_4$-$PTFOA_1$/PS still maintains similar morphology as before, and the porous structure can be clearly observed on both beads and fibers in the magnified image (Figure S9b), which indicates that the pristine structure was not destroyed by the pretreatments and UV photografting.

Table S1 Electrospinning solution compositions of the PS fibrous membranes.

	DMSO/CB (v/v)	**PS Conc (mg/mL)**
D20-1	20/80	100
D20-2	20/80	200
D20-3	20/80	300
D0T-3	0/100	300
D40-3	40/60	300

(T: Tetrabutylammonium perchlorate, a kind of organic salt for enhancing the conductivity of the solutions.)

Table S2 Physical properties of various oils used for oil/water separations [S3].

Oil	**Density ($g\ cm^{-3}$, 20°C)**	**Viscosity (mPa s, 20°C)**	**Surface tension ($dyne\ cm^{-1}$)**
Hexane	0.66	0.33	18.4
Iso-octane	0.69	0.53	20.5
Hexadecane	0.77	3.38	27.2
Liquid paraffin	0.86-0.91	110-230	~35
Plant oil	0.92	72-500	-

References

[S1] Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Mussel-inspired surface chemistry for multifunctional coatings. *Science*, **2007**, 318, 426-430.

[S2] Leeden, V. D.; Mieke, C. Are conformational changes, induced by osmotic pressure variations, the underlying mechanism of controlling the adhesive activity of mussel adhesive proteins. *Langmuir*, **2005**, 21, 11373-11379.

[S3] Huber M L, NIST Thermophysical properties of hydrocarbon mixtures database (SUPERTRAPP), version 3.2, 2007.