Supporting Information

Patterned fouling-free membrane with controllable wettability for ultrafast oil/water separation and liquid-liquid extraction

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Video S1 the hexane/water separation with the big pore size (Diameter: 1 cm) glass tube by the patterned membrane (pore size: 0.22 μm)

Video S2 the hexane/water separation with the small pore size (Diameter: 0.5 cm) glass tube by the patterned membrane (pore size: 0.22 μm)

Materials and Experiments

Materials

The petroleum ether, DMF, methylbenzene, n-heptane, n-hexane, CCl_4, oil red, and 4-Benzoylamino-2, 5-diethoxybenzenediazonium chloride hemi (zinc chloride) salt particles (Fast blue BB salt) were obtained from Aladdin Co., Ltd (China). The PP membrane (different pore size: 0.22 μm, 1.2 μm, and 5 μm, what is not specifically indicated in the text refers to the PP membrane with a pore size of 0.22 μm) were obtained from the EMD Millipore Corporation.

Experiments

Preparation of the uniform superhydrophilic PP porous membrane

The hydrophobic PP membrane (pore size: 0.22 μm) was immersed in the DA solution (2 mg mL^{-1} DA, 25 °C, 10 mM tris, pH = 8.5) with H_2O_2 (19.6 × 10^{-3} mol/L)/$CuSO_4$ (5 × 10^{-3} mol/L) for 50 min, repeating the process for three times to form the superhydrophilic PP porous membrane.

Oil/water separation

For traditional oil/water separation, the pre-wetted membranes (radius: 4.7 cm) were fixed between two glass tubes. The diameter of the tube was 4 cm. The oil/water mixtures (petroleum ether (50 mL)-water (50 mL)) were poured onto the device. For LIPPM, a piece of lower-layer liquid infused membrane (radius: 3.8 cm) was put into the glass tube with different pore size (1.0 cm and 0.5 cm), where contains 200 mL immiscible oil-water mixture (50 v/v%). Opening the rubber plug for separation, the low-layer liquid flowed from pore quickly, where the upper-layer liquid was blocked by the lower-layer liquid infused membrane finally. **The filtered water was stirred violent to form a homogeneous solution and the absorption was analyzed using an UV-vis spectrometer.**

Antifouling experiments

Suspension of fast blue BB salt particles (0.5 mg/mL in water, 20 °C) was applied to separation (traditional and LIPPM). For traditional oil/water separation, the 100 mL hexane/suspension mixture (50 v/v%) was applied to the water pre-wetted superhydrophilic PP membrane (pore size: 0.22 μm). For LIPPM, a piece of water and hexane infused patterned membrane (radius: 3.8 cm, pore size: 0.22 μm) was put into the big pore size glass tube (diameter: 1.0 cm), where contained 200 mL hexane/suspension mixture (50 v/v%).

Liquid-liquid extraction

A new separatory funnel (500 mL) with a flat platform was used for extraction. A piece of water and oil co-infused patterned membrane (Radius: 3.8 cm) put into the separatory funnel containing oil (150 mL, dyed by oil red)–water (150 mL) mixture for extraction. The process was recorded using Canon IXUS 115 HS digital camera.

Characterization

The FT-IR spectra were operated by the Bruker Vertex 70 spectrometer at a nominal resolution of 2 cm^{-1}. All measurements of the contact angles were obtained by Drop Shape Analysis DSA10 (Krüss Gmbh, Germany) at ambient temperature with a droplet of 5 μL in volume. The morphology and EDS were obtained by scanning electron microscope (SEM, Philips XL30 ESEM FEG).

Table S1 The pore size of different porous membranes.

Membranes	Pore size (μm)
PP1	0.22
PP2	1.2
PP3	5.0

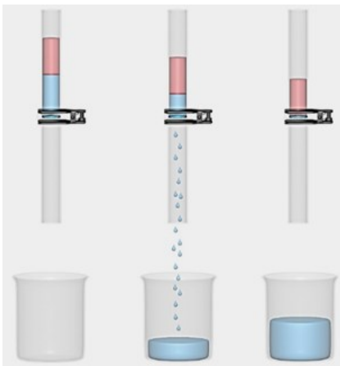

Fig. S1 The schematic of traditional oil/water filtration.

Fig. S2 The water drops (dyed by reactive red) on the hydrophobic dots and superhydrophilic background.

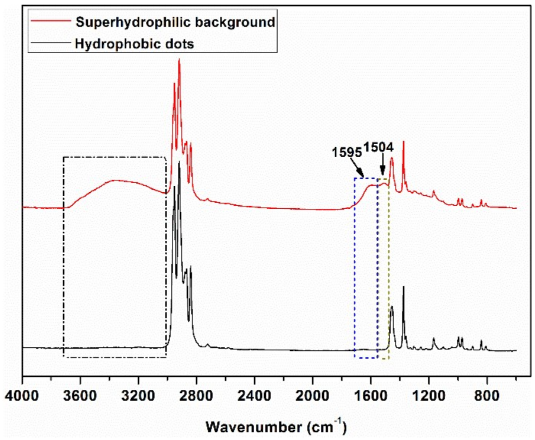

Fig. S3 The FTIR spectra of the patterned porous membrane's different region.

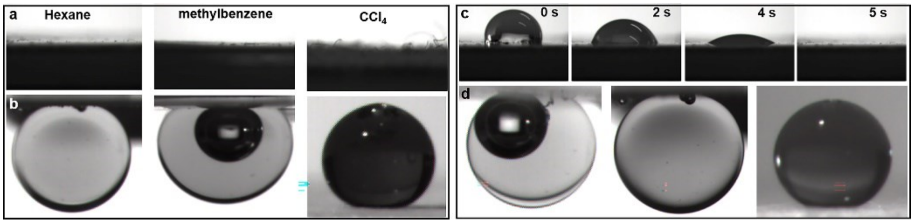

Fig. S4 The contact angle of different regions of the patterned porous membrane. (a) The oil contact angle and (b) under-oil water contact angle of the hydrophobic dots. (c) The water contact angle and (d) underwater oil (hexane, methylbenzene, and CCl_4) contact angle of the superhydrophilic background.

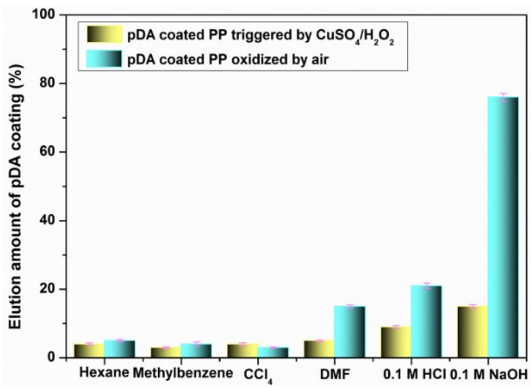

Fig. S5 Elution amount of the patterned PP porous membrane fabricated by different procedure immersed in different solutions.

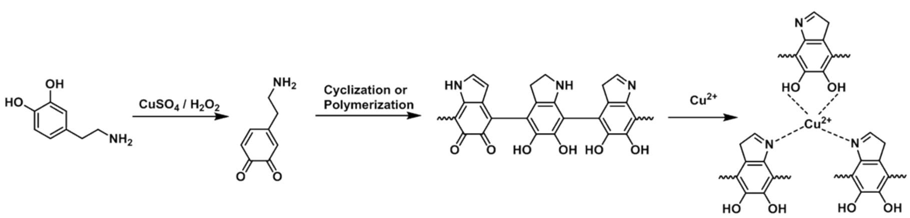

Fig. S6 Illustration of the reduction of C-H during the process of dopamine polymerization and the chelation after dopamine polymerization.

The chemical stability of membrane is essential for its practical application. The hydrophobic-superhydrophilic patterned PP porous membrane fabricated by using $CuSO_4/H_2O_2$ as a trigger has the ability to resist alkali, acid, and organic solvents. To investigate the chemical stability, the patterned porous membranes fabricated by using $CuSO_4/H_2O_2$ as a trigger and the membrane developed through oxidation in air (without the trigger) were immersed in strong alkali, acid, and different oils for 3 h. The elution amounts were tested to evaluate the stability of the membrane. Fig. S5 (ESI†) shows that the elution amount of membrane fabricated by air oxidation method increased dramatically with the polarity increase of the oils. However, the patterned porous membrane triggered by the $CuSO_4/H_2O_2$ hardly elutes with the oils. The results confirm that the patterned porous membrane developed by using $CuSO_4/H_2O_2$ as a trigger exhibited improved stability in alkali and acid environments. The improved stability may be ascribed to the reduced C-H ratio and chelation between Cu^{2+} and amine and imine groups of pDA (Fig. S6, ESI†).

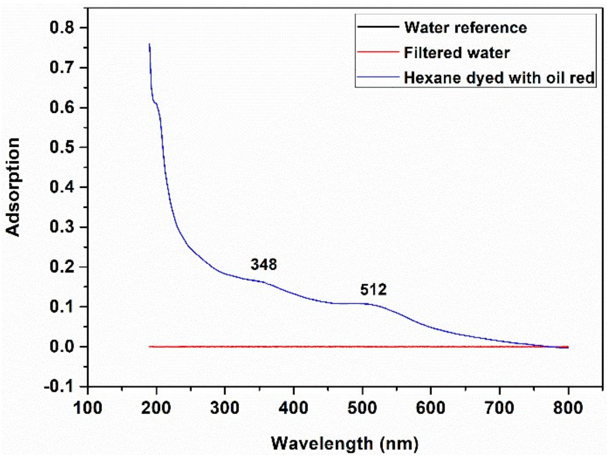

Fig. S7 UV-visible spectroscopy absorption data for water reference, filtered water, and hexane dyed with oil-red.

The oil red dyed hexane has typical peaks of absorption at 348 nm and 512 nm, which is not seen in the filtered sample (Fig. S7 ESI†). These absorption spectra prove that the filtered sample only contains water without hexane, which demonstrates the high efficiency of the separation.

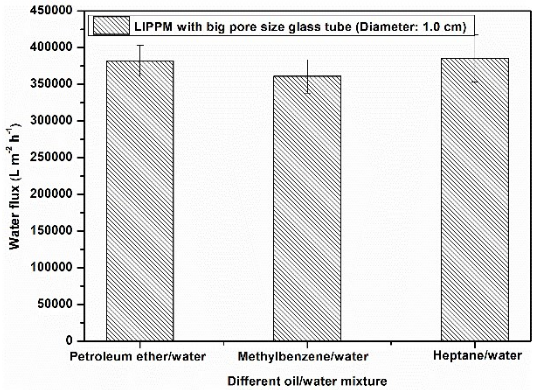

Fig. S8 The water flux results of LIPPM (patterned PP membrane, pore size: 0.22 µm) for different oil/water mixture.

Fig. S9 The pore clogging experiments for traditional filtration. (a) The water pre-wetted superhydrophilic PP patterned membrane (pore size: 0.22 µm) separates the hexane (dyed by Oil Red)-water (Fast Blue BB salt solution, yellow) mixture (50 mL-50 mL) by traditional filtration method. The colour of filtrates (b) before filtration (original solution) and after filtration with different recycles (1, 2, 3) for traditional filtration. (d) The flux of traditional filtration with increased recycles.

For traditional filtration (Fig. S9a, ESI†), flowing a hexane/suspension mixture through a water pre-wetted superhydrophilic PP porous membrane (pore size: 0.22 µm) leaves salt particles suspended both in and around the pores. Increasing with the recycle, more and more particles are suspended on the surface, inducing a quick decline of the flux from 46 L (m^{-2} h^{-1}) (original without microparticles) to 19 L (m^{-2} h^{-1}) (recycle 1) to 13 L (m^{-2} h^{-1}) (recycle 2) to 7 L (m^{-2} h^{-1}) (recycle 3) (Fig. S9c, ESI†). Because of the deposition of the particles on the membrane, the color of the filtrates becomes lighter and lighter with increased recycles (Fig. S9b, ESI†).

Fig. S10 The pore clogging experiments for LIIFPM system. (a) The liquids-infused patterned PP porous membrane (pore size: 0.22 μm) separates the hexane (dyed by Oil Red)-water (Fast Blue BB salt solution, yellow) mixture (100 mL-100 mL) by LIIFPM system. The colour of filtrates (b) before filtration (original solution) and after filtration with different recycles (5, 10, 20) for LIIFPM system. c) The flux of LIIFPM system with increased recycles.

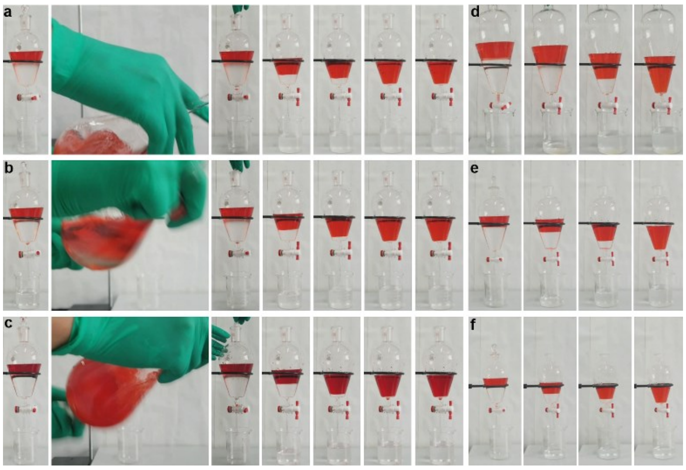

Fig. S11 The LIPPM system is used in real-world extraction in different system, (a) hexane (dyed by oil red)/water, (b) petroleum ether (dyed by oil red)/water, (c) methylbenzene (dyed by oil red)/water. The separatory funnel with different volume (1000 mL (d), 500 mL (e), 250 mL (f)) is used for hexane (dyed by oil red)-water extraction.

The LIPPM system with excellent oil/water separation ability, outstanding floatability, and self-gating behavior can be developed to a movable gate for liquid-liquid extraction. The conventional extraction device is designed with a flat platform for application. The advanced device combined with the LIPPM can realize the extraction. In this paper, we define the upper layer as the extract phase. As shown in Fig. S11a, the new separatory funnel has a hexane (150 mL)-water (150 mL) mixture. Vigorous rocking for extraction, the solute transferred from the raffinate into extract. After vigorous rocking, a piece of liquids-infused patterned PP membrane was put into the device and it could float at the hexane-water interface naturally. Open the switch for separation, the water flowed out the separatory funnel from the bottom slowly. At last, the liquids-infused patterned PP membrane stayed at the flat platform like a gate to close the pore achieving the separation. The LIIFPM system brought a lot of convenience to this process. A variety of immiscible oil/water mixtures, including petroleum ether/water (Fig. S11b) and methylbenzene/water (Fig. S11c), have been successfully extracted through such process. Remarkably, the new separatory funnel with different volume (1000 mL, 500 mL, and 250 mL) can be designed for hexane-water extraction successfully (Fig. S11d-f).