

A Liquid-based Janus porous membrane for convenient liquid-liquid extraction and immiscible oil/water separation

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Video S1 For real-world extraction, petroleum ether (dyed by oil red)/water extraction

Video S2 Oil/water separation, hexane (dyed by oil red)/water separation

1. Experiments

1.1. Materials

The Dopamine hydrochloride (DA), Tris (hydroxymethyl) aminomethane (tris), PVA with a number-average molecular weight of 16 000 (98% hydrolyzed), and GA aqueous solution (50 wt% in water) were obtained from Sigma-Aldrich (USA). HCl (37 wt%, extra pure grade), petroleum ether, ethyl acetate, dichloromethane, ethanol, oil red, and Sudan Red were obtained from Aladdin Co., Ltd (China). The PP non-woven fabric (PP) was obtained from Beijing North Dawn Membrane Separation Technology Corporation.

1.2. Experimental methods

1.2.1. Fabrication of the Janus porous membrane

The clean PP was pre-wetted by the ethanol for 10 s. The residual ethanol on the surface was absorbed by a filter paper. The membrane was put on the surface of the DA solution (2 mg mL⁻¹, 10 mM tris, pH=8.5) at 60 °C. The membrane was took out carefully after 1 h and rinsed by the deionized water immediately. The as-prepared membrane was dried in a vacuum oven. The PVA solutions (4%wt) were prepared by dissolving PVA powder in deionized water at 90 °C. After cooling to room

temperature, the pH of the PVA aqueous solutions was corrected to 2 with HCl (as a catalyst). Then the hydrophilic surface of the membrane was immersed into PVA solutions at ambient temperature for 30 min, allowing for the PVA solutions completely wetting the hydrophilic surface. Subsequently, the PVA wetted membranes were taken out and again immersed into 20 mL of GA solution at ambient temperature for 6 h. Finally, the Janus porous membranes were washed in water and ethanol several times and then dried under vacuum before use.

1.2.2. Contact angle, SEM, FTIR Measurement

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

1.2.3. Pore size, intrusion height, and stability

Different Janus porous membranes were operated by Capillary Flow Porometer (CFP-1500AE) to test the pore size. The intrusion height of different liquids through the Janus porous membranes was characterized by measuring the maximum height of liquids that could support. To measure the oils' intrusion height, the superhydrophilic surface of the Janus porous membrane is wetted by water firstly. Similarly, the hydrophobic surface was wetted by dichloromethane to measure the water's intrusion height. The pH stability of the Janus porous membranes was evaluated by immersing the membranes (2 cm \times 2 cm) in 10 mL aqueous solutions with different pH values

for 24 h and water and underwater oil (dichloromethane, dyed by oil red) contact angles were then measured after drying the membranes. The solvent resistance test was performed by immersing Janus porous membranes (2 cm × 2 cm) in 10 mL of various organic solvents for 24 h. Water contact angles of different surface were then measured after drying the membranes. The tested solvents include dimethylformamide (DMF), ethyl acetate, Toluene, dichloromethane (DCM), tetrahydrofuran (THF), hexane, petroleum ether (PE), and Actone.

1.2.4. Oil-water separation

A glass syringe with a diameter of 4 cm was used to perform the oil/water separation experiment. A piece of Janus porous membrane (Radius: 3 cm) was put into the syringe with 20 mL–20 mL (ethyl acetate-water, petroleum ether-water, and water-dichloromethane) mixtures. Opening the stopper for separation, the water would be separated from the mixture, where the membrane acted as a gate to block the hole perfectly stopping the process at the end. The oil content in water was determined by TOC, while the water content in oil was determined by a Karl Fischer titrator.

1.2.5. Real-world extraction

A new separatory funnel (500 mL) with a flat platform was used for extraction. A piece of Janus porous membrane (Radius: 3 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. The absorption concentration was measured by a UV-vis spectrometer (SHIMADZU 1800). The oil red or Sudan Red content was obtained by calculating the absorbance.

2. Result and discussion

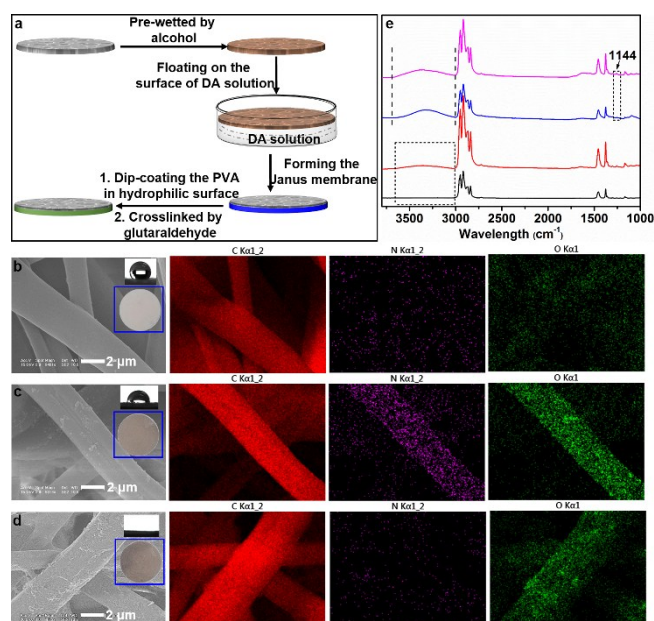


Fig. 1 (a) Schematic diagram of the process to fabricate JPM. The morphology, color, EDS mapping images, and WCA of JPM's hydrophobic surface (b), hydrophilic surface with polydopamine (pDA) (c), and superhydrophilic surface with 5%wt crosslinked PVA (d). (e) The FTIR of JPM's different surface (black line: hydrophobic surface; red line: hydrophilic surface with pDA; blue line: superhydrophilic surface with 5%wt PVA; pink line: superhydrophilic surface with 5%wt crosslinked PVA).

The as-prepared composite membrane exhibits significant differences in wettability on opposite surfaces. The side modified with pDA becomes significantly hydrophilic with a water contact angle (WCA) of 89 ° (Fig. 1c). Subsequently, the pDA deposited surface is readily modified by PVA followed by crosslinking. This induced the abrupt decrease in the WCA, representing the superhydrophilicity of the surface after modification with the crosslinked PVA (c-PVA) (Fig. 1d). The WCA of the opposite side remained at approximately 138°, which revealed that the modification remained selective, and the other side is still hydrophobic (Fig. 1b). The respective surfaces of the JPM can be easily distinguished by their colors, i.e., white for a hydrophobic surface, and dark brown for both hydrophilic surfaces modified with pDA as well as superhydrophilic surfaces with crosslinked PVA, as shown in Fig. 1b–d.

Scanning electron microscopy (SEM) images verify that the morphologies of the two surfaces of the JPM exhibit remarkable differences. Fig. 1c shows that the pDA particles were successfully deposited on the surface, which is different from the smooth hydrophobic surface (Fig. 1b). The crosslinked PVA uniformly covers the hydrophilic surface and enhances the surface roughness (Fig. 1d). The surface chemical composition was investigated using an energy dispersive spectroscope (EDS) (Fig. 1b–d). Compared with the hydrophobic surface, elemental N and O appear on the pDA-modified surface. In the case of a superhydrophilic surface (modified by c-PVA), the weak signal of N reveals that the surface of pDA is largely covered by c-PVA. Such a remarkable difference in the surface roughness and chemical composition contributes to the anisotropic wettability of the JPM. The Fourier transform infrared (FTIR) spectra recorded for JPM further confirmed the structural difference of the JPM on the different sides (Fig. 1e).

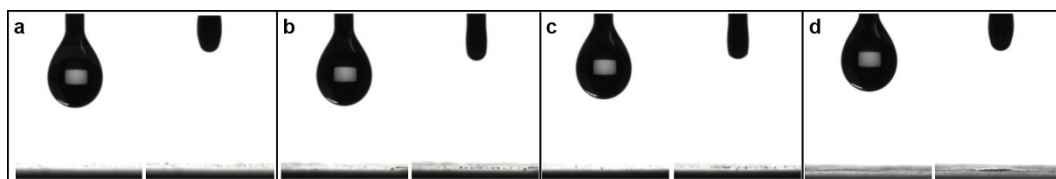


Fig. S1 When the superhydrophilic surface is infused by water, the immiscible oil (CCl_4 , hexane, petroleum ether, dichloromethane (DCM), methylbenzene) contact angle.

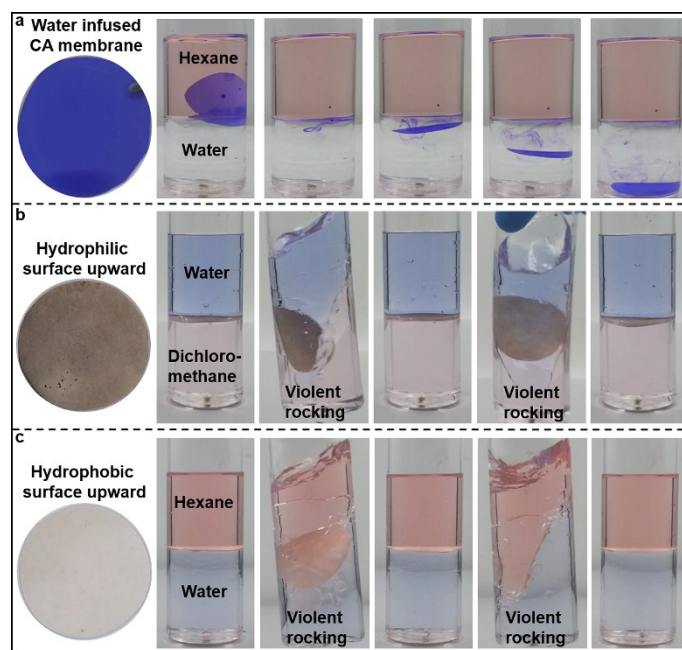


Fig. S2 (a) The water (dyed by methyl blue)-infused CA membrane penetrates the hexane (dyed by oil red)-water (dyed by methyl blue) interface and sinks in the bottom. (b) The water and dichloromethane infused Janus porous membrane can stably float at the water (dyed by methyl blue)-dichloromethane (dyed by oil red) interface with the superhydrophilic surface (dark brown) upward after several times of violent rocking. (c) The hexane and water infused Janus porous membrane can stably float at the hexane (dyed by oil red)-water (dyed by methyl blue) interface with the hydrophobic surface (white) upward after several times of violent rocking.

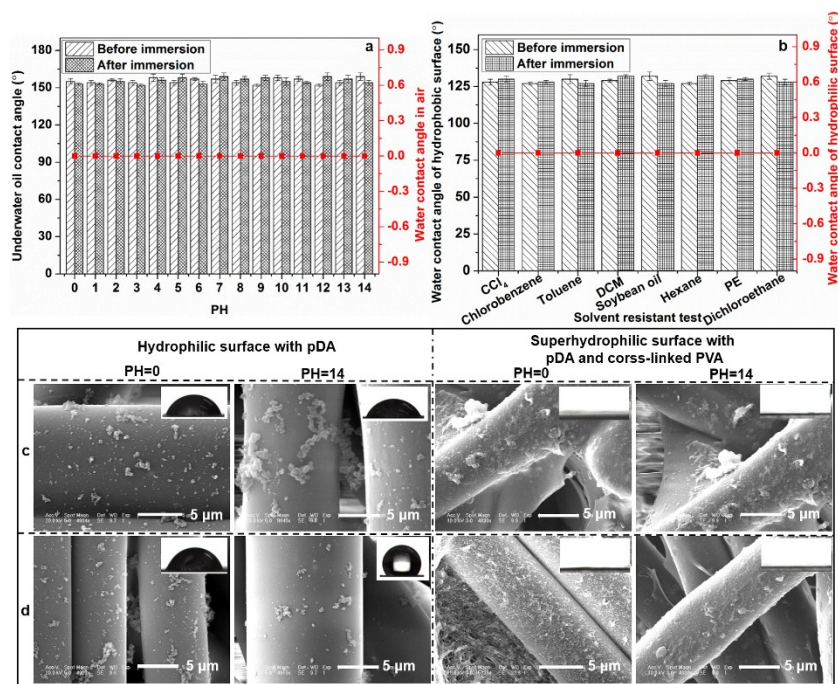


Fig. S3 Study of stability of the Janus porous membrane. (a) Variation of WCA and underwater oil (hexane) CA of the superhydrophilic surface of Janus porous membrane after immersing in the solution with different pH values for 24 h. (b) The WCA of the Janus porous membrane's different surface after immersing in various organic solvents for 24 h. The wettability and morphology of the pDA modified hydrophilic surface and pDA-PVA coated superhydrophilic surface before (c) and after (d) immersion in highly acid and alkaline environment 24 h.

Fig. S3a shows the superhydrophilic surface of the membrane keeps their superhydrophilic and underwater superoleophobic property with zero WCA and $>150^\circ$ underwater oil CA after being immersed in different pH solutions for 24 h, exhibiting that the Janus porous membrane has superior stability against acid and alkali. The solvent resistant ability of the Janus porous membrane was tested by immersing the membrane in various organic solvents overnight and WCA of different surface was measured. As shown in Fig. S3b, the Janus porous membrane retains wettability property, where no obvious change of WCA is observed after immersion. This result confirms the excellent solvent resistance ability of the Janus porous membrane. The hydrophobic surface of the Janus porous membrane is inert PP which is stable under different conditions. For the pDA modified hydrophilic surface, the pDA shows the superior stability against acid conditions, however, it is unstable in

strong alkaline conditions. SEM observation shows that the pDA in hydrophilic surface has been partially dissolved in alkali and is maintained well in acid environment (Fig. S3c, d). Therefore, the WCA of the pDA modified surface is maintained after immersion in high acid solution and improved in high alkaline condition (Fig. S3c, d). Further coated by PVA and crosslinked by glutaraldehyde (GA), the Janus porous membrane has the enhanced resistance to acid, alkali, and solvent, where the surface morphology and wettability nearly have no obvious change in high alkaline, acidic, and different solvents environment (Fig. S3c, d). The enhanced stability may be attributed to the covalent bond bridged multiple crosslinked networks by PVA and pDA.¹ The pDA, possession a large amount of -OH, can co-crosslink with the PVA by the GA to form covalent bond bridged multiple crosslinked networks, which is same with the PVA coated filter paper. Thus, the Janus porous membrane owns inert PP surface and multiple crosslinked networks has good stability to resist highly acid, alkali, and organic solvents.



Fig. S4 The original separatory funnel (500 mL), the new separatory funnel (intelligent device, 500 mL), and the glass syringe (from left to right).

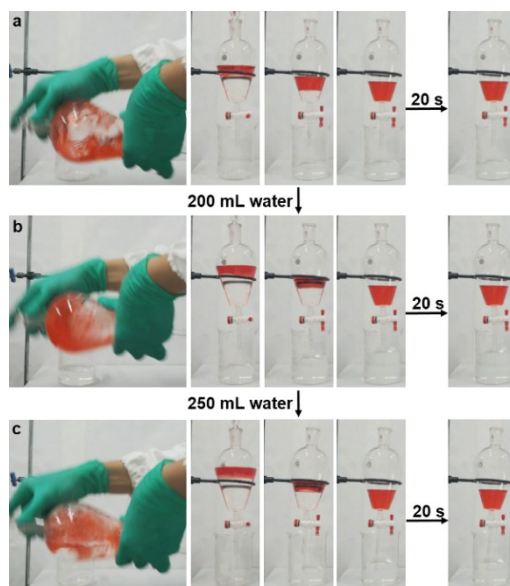


Fig. S5 The continuous extraction for petroleum ether (dyed by oil red)-water system with different solution ratio, 100 mL-150 mL (a), 100 mL-200 mL (b), 100 mL-250 mL (c).

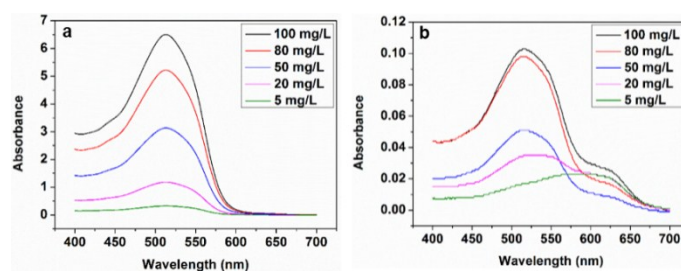


Fig. S6 (a) The absorbance of the original oil red (different concentration of the oil red dyed petroleum ether, 100 mg/L, 80 mg/L, 50 mg/L, 20 mg/L, 5 mg/L). (b) After extraction (different concentration of the oil red dyed petroleum ether-water mixtures), the absorbance of the oil red by the Janus membrane.

Table S1 The original concentration of the oil red dyed petroleum ether (100 mg/L, 80 mg/L, 50 mg/L, 20 mg/L, 5 mg/L), and the concentration absorbed by the Janus membrane calculates from UV-vis absorbance data.

Original concentration	Concentration absorbed by the Janus membrane
100 mg/L	0.079 mg/L
80 mg/L	0.075 mg/L
50 mg/L	0.041 mg/L
20 mg/L	0.03 mg/L
5 mg/L	0.0177 mg/L

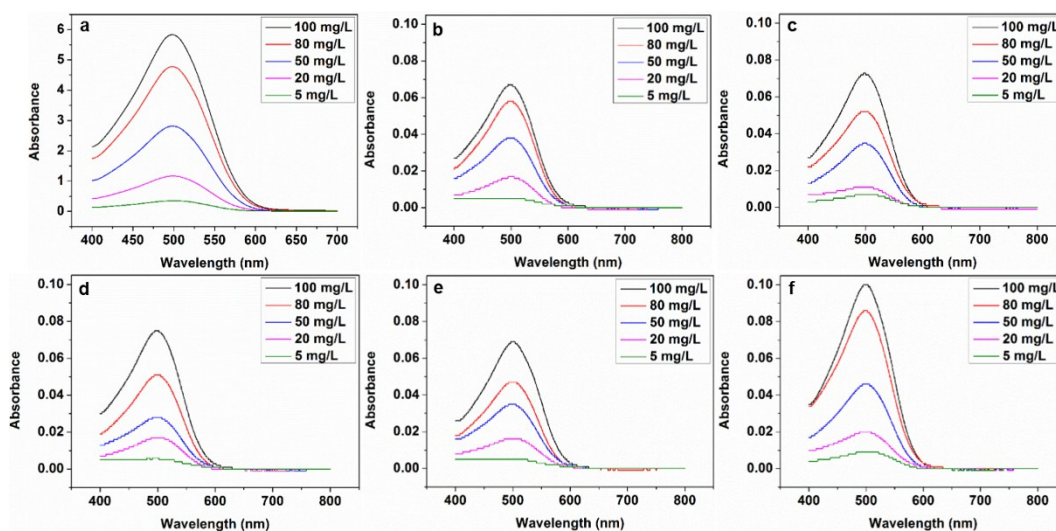


Fig. S7 (a) The absorbance of the original Sudan Red (different concentration of the Sudan Red dyed water, 100 mg/L, 80 mg/L, 50 mg/L, 20 mg/L, 5 mg/L). After extraction (different concentration of the Sudan Red dyed water- dichloromethane mixtures), the absorbance of the Sudan Red by different Janus membrane (b. 2% PVA coated Janus membrane; c. 4% PVA coated Janus membrane; d. 6% PVA coated Janus membrane; e. 8% PVA coated Janus membrane; f. 10% PVA coated Janus membrane).

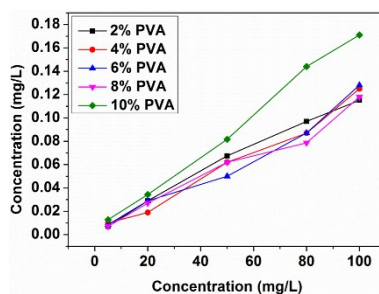


Fig. S8 The concentration absorbed by different Janus membranes calculates from UV-vis absorbance data.

For real extraction, the adsorption of the JPM is an inevitable concern. The UV-visible spectroscopy absorption data, shown in Fig. S6 and S7 (ESI†), determined the specific amount of absorbed solute (oil red or Sudan Red) by the JPM after the extraction. Different concentrations of extraction solution (oil red-dyed petroleum ether or Sudan Red-dyed water) were used for real extraction. In the petroleum ether–water system, the oil red-dyed petroleum ether samples had typical peaks of absorption at 512 nm. After the extraction, the solution absorbed by the JPM exhibited a weak absorption peak at 512 nm, which indicates that the concentration is far below the original concentration (Fig. 3e). For the water (dyed by Sudan Red)–dichloromethane system, the Sudan Red-dyed water exhibited a typical peak at approximately 485 nm. The JPMs with different concentrations of PVA in the superhydrophilic surface were applied for extraction (Fig. S8, ESI†). Weak absorption peaks corresponded to the minute absorption concentrations (Fig. 3f). The absorption concentrations after extraction were found to be three times lower than the original concentrations in the different systems, showing the strong potential of JPM to be used for an efficient real extraction process.

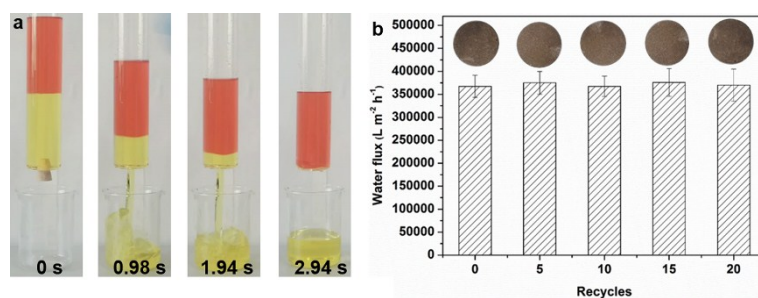


Fig. S9 The antifouling and recycle property. (a) The hexane and water infused Janus porous membrane (pore size: 1.0 μm) separates the hexane (dyed by oil red)-water suspension (Fast Blue BB salt solution, yellow) mixture (100 mL-100 mL). (b) The color of water-infused superhydrophilic surface and water flux with increased separation recycles (0, 5, 10, 15, 20).

The Janus porous membrane is independent to the pore size of the membrane possession the antifouling property for ultrafast oil/water separation. To test the antifouling and recycle property of the LBJPM, as shown in Fig. S9a, we used the same hexane and water infused Janus porous membrane (pore size: 1.0 μm) to ultrafast separate the hexane-water suspension (0.5% Fast Blue BB salt solution with a diameter of $\sim 2.5 \mu\text{m}$) mixture. As the number of recycles increasing, the water-infused superhydrophilic surface do not change (Fig. S9b). Meanwhile, the ultrahigh flux is about the same with the increased recycles which is up to 20 (Fig. S9b), indicating that the LBJPM can avoid the clogging with an antifouling property for continuous and ultrafast oil/water separation.

Reference

1. J.-B. Fan, Y. Y. Song, S. T. Wang, J. X. Meng, G. Yang, X. L. Guo, L. Feng and L. Jiang, *Adv. Funct. Mater.*, 2015, **25**, 5368.