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Electronic Supplementary Information (ESI)

Crown Ether Modified Membranes for Na⁺-Responsive Controllable Emulsion

Separation suitable for hyper-saline environments

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1. Effect of the thickness on the separation efficiency and the flow rate

The thickness of the membrane was controlled by changing the amount of B15C5 modification on the membrane, that is, the B15C5 concentration in acetone. Except for 50 mg B15C5/50mL acetone in the manuscript, two other concentrations were used including 25 and 100 mg/50mL. And we measured the water removal efficiency and flux of the three membranes for the separation of toluenen-in-water emulsion. When the concentration was 25 mg/50mL, both of the water removal efficiency and flux were low, only 92.12 % and 29.58 L/m²h. It is probably that the hydrophobic substrate was exposed to the surface due to insufficient amount of B15C5 modification. While for 100 mg/50mL, compared with 50 mg/50mL, there was a slight variation in separation efficiency and flux of the two membranes, which meant that after the substrate being covered with the modifier, the thickness of the modifier may have little effect on separation performance of the as-prepared membrane.



Fig. S1 Effect of the thickness on the separation efficiency and the flow rate

2. FTIR Spectrum of Pure B15C5

The FTIR spectrum of pure B15C5 is observed in Fig. S1. The characteristic absorption bands of ether bond C–O–C appears at 1230 and 1120 cm⁻¹, and the characteristic absorption bands of the benzene ring of B15C5 exhibit at 1593, 1506 and 1454 cm⁻¹. This spectrum agrees well with the FTIR results of B15C5-coated membrane.



Fig. S2 FTIR spectrum of pure B15C5.

3. UOCA of the B15C5-coated membrane

The water used here is deionized water. UOCA of the B15C5-coated membrane is 0°, indicating that the as-prepared membrane was underwater superoleophilic. Besides, the Na⁺-binding B15C5-coated membrane was also put in deionized water to observe its UOCA. In the initial state, the UOCA of the membrane was about 152°, similar to the membrane in 36 % NaCl solution. However, about one minute later, the UOCA started to decrease, finally it stabilized at about 31.9°. This result indicated that there are some Na⁺ left on the membrane, binding with B15C5 in an irreversible way. While it also showed that the as-prepared membrane can adjust its wetting behavior according to the surrounding environment, and this superwetting switching is fast.



Fig. S3 a) UOCA of B15C5-coated membrane; b) UOCA of the Na⁺-binding B15C5coated membrane in deionized water for about one minute

4. Variation of UOCA as a function of Na⁺ concentration

When Na⁺ concentration was less than 0.1 %, UOCA of the Na⁺-binding B15C5coated membrane was always 0°, showing underwater superoleophilic at this time. As Na⁺ concentration increased from 0.1 % to 1 %, UOCA increased sharply from 0° to about 130°, realizing the superwetting switching from underwater superoleophilicity to underwater superoleophobicity. After that, it changed slightly and almost stabilized at 3 % with UOCA about 152°. Not only WCAs but also UOCAs of the as-prepared membrane varied as a function of Na⁺ concentration, further approving the Na⁺responsive superwetting switching of the as-prepared membrane.



Fig. S4 Variation of UOCA as a function of Na⁺ concentration

5. The wetting properties of original and roughened PTFE substrates

The light oil we used here was toluene, and water here was deionized water. WCAs in air of PTFE substrate and roughened substrate were 102.1° and 123.8°, and UOCAs of the two membranes were about 59.7° and 40.8°. The results showed that roughened substrate without B15C5 modification could not realize the highly hydrophobic/underwater superoleophilic wettability. Therefore, it was the combination of the modifier B15C5 and PTFE substrate that contributed to the superwetting switching of the as-prepared material.



Fig. S5 The wetting properties of original and roughened PTFE substrates

6. Feasibility of other hydrophobic or hydrophilic substrates

The original GF, nylon and PP membranes were superhydrophilic (~0°), highly superdrophilic (~21.5°) and hydrophobic (~121.9°), respectively. After B15C5 modification, the B15C5-coated GF membrane still exhibited superhydrophilic probably due to the extreme superhydrophilicity of the GF substrate and instability of modification on it. Besides, WCAs of B15C5-coated nylon membranes are about 73.1°, showing low hydrophobicity of B15C5. After immersing into 3 % NaCl solution, the as-perpared membrane changed to be superhydrophilic. While as for PP substrates, similar to PTFE substrates, the hydrophobicity was increased from about 121.9° to about 140.1° after B15C5 modification, and the WCAs changed to about 26.1° in the presence of Na⁺ on the membranes.



Fig. S6 Feasibility of other hydrophobic or hydrophilic substrates

7. Five successive reversible wettability transition cycles

The recyclability performance of the as-prepared membrane was also examined through five successive reversible wettability transition cycles. As shown in Fig. S2, the contact angles in the mass change slightly, while the hydrophobicity decreases more than others when Na⁺ falls off firstly, owing to the irreversible complexation between crown ethers and a small portion of Na⁺. But the membrane still exhibits highly hydrophobic or highly hydrophilic after five successive separation cycles, indicating a satisfactory reusability. And it is noted that the Na⁺-responsive wettability transition of the membrane is swift.



Fig. S7 Wettability transition via five successive reversible cycles.

8. The Influence of Other Ions on Surface Wettability

In order to explore the influence of other ions on surface wettability, K^+ , Ca^{2+} , Cu^{2+} , Ni^{2+} , Li^+ and Mg^{2+} were also tested as responsive ions, and the water contact angles (WCAs) of the B15C5-coated membrane after soaking in saturated KCl (34 %), CaCl₂ (74.5 %), CuSO₄ (23 %), NiSO₄ (32 %), LiCl (67 %) and MgCl₂ (55 %) solutions are shown in Fig. S. But there is not an obvious change in the WCAs due to the weak bonding force between these ions and B15C5, which further confirms the Na⁺-responsive property of the as-prepared membrane.



Fig. S8 WCAs of the B15C5-coated membrane after soaking in saturated KCl (34 %), $CaCl_2$ (74.5 %), $CuSO_4$ (23 %), $NiSO_4$ (32 %), LiCl (67 %) and $MgCl_2$ (55 %) solutions.

9. Experimental devices used in emulsion separation

The oil/water separation experiment procedure was carried out as shown in Fig. S4. The as-prepared membrane was fixed in a filtration device and the stabilized water-inoil emulsion was poured onto the surface. Owing to the hydrophobicity of B15C5, oil permeates through the membrane quickly and drops into a conical flask below, while water is repelled and kept above the membrane. No external force is employed during the separation procedure except for gravity. Besides, the membrane is able to separate oil-in-water emulsions that contain Na⁺ (concentration greater than 1 %) without additional equipments. After forming polar and positive charged Na⁺-B15C5 coordination complex, the water retention capacity of the as-prepared membrane is reduced significantly, and water goes through the membrane while oil is retained above.



Fig. S9 Experimental devices used in emulsion separation.

10. Separation capacity of various kinds of emulsions with different surfactants

None of emulsified droplets are observed in the optical images of the filtrates collected from emulsions stabilized by Span 80, Tween 20 and SDS in comparison with the whole view composed of homodispersed droplets before filtration. As for the filtrate from CTAB-stabilized oil-in-water emulsion, the number of droplets decreases significantly though there are some small droplets remained after filtration. The optical microscopy images of the feed and the filtrate demonstrate the effective separation for both stabilized oil-in-water and water-in-oil emulsions.



Fig. S10. Optical images of the feed emulsions with different surfactants and corresponding filtrates.

11. The flux recovery rate of the as-prepared membrane

We measured the mass of feeds and filtrates of different surfactant stabilized emulsions, including toluene-in-water emulsion with Tween-20, toluene-in-water emulsion with SDS, toluene-in-water emulsion with CTAB and water-in-toluene emulsion with Span-80. The flux recovery rate can be calculated by the mass of feeds and filtrates. The result showed that the flux recovery rates of the four kinds of emulsions with different surfactant were 89.51 %, 90.72 %, 81.06 % and 89.6 %, respectively. It was obvious to see that the flux recovery rate of toluene-in-water emulsion with CTAB was the lowest among them, which may attribute to the hydrophobicity enhancement of the membrane surface due to the presence of CTAB. Thus the penetration resistance of water will increase. In the end, a small part of the water may remain on the surface of the membrane, leading to a lower flux recovery rate of the emulsions, all around 90 %, were relatively large, showing an excellent flux recovery performance of the as-prepared membrane.



Fig. S11. The flux recovery rate of the as-prepared membrane

12. AFM images of the membrane before and after five successive separation cycles

In order to obtain the average roughness of the full view, several different areas of each membrane were observed and the Rq was taken average. As shown in AFM images below, the average Rq of the as-prepared membrane before and after five emulsion separation cycles was 71.5 nm and 55.7 nm, respectively. Since there is no big difference among these areas, the average Rq could be the representative roughness of the membranes. The AFM results further proved that the surface roughness of the as-prepared membrane did not decrease a lot after five cycles. And due to the impact and friction of fluid, the rough structure of membrane surface after use became a little smoother and more even.



Fig. S12. AFM images of the membrane before and after five successive separation cycles

13. The separation efficiency and flux of five successive emulsion separation cycles

After five successive emulsion separation cycles, the separation efficiencies of oilin-water and water-in-oil emulsions were 98.93 % and 97.9 %, and the fluxes of them were 45.51 L/m²h and 41.24 L/m²h. As the times of separation increased, the overall separation efficiency gradually decreased, while flux gradually increased. But the material still remained a relatively great separation performance after five cycles. Besides, it was obvious to see that the separation performance in the third time declined a lot, which probably because some Na⁺ interacted with the crown ether in an irreversible way. When the membrane was put back to low-Na⁺ environment, as mentioned above , the hydrophobicity cannot be restored to its original state, leading to the low separation efficiency and flux.



Fig. S13. The separation efficiency and flux of five successive emulsion separation cycles

14. Separation performance of the as-prepared membrane after ultrasound

From the optical image we can see that the filtrate collected from the emulsion was still opaque. And the separation efficiency decreased sharply from about 98.71 % to about 42.68 %, which indicated the poor mechanical stability. But after a simple spraying process, the separation efficiency will be restored to the original state (about 98.7 %).



Fig. S14. Separation performance of the as-prepared membrane after ultrasound and

after respraying.

15. oil contact angles of B15C5-coated mesh after acid/alkaline solution treatment

The wettability transition of oil on the B15C5-coated membrane is also not affected. Thus it is further confirmed that whether in acidic or alkaline environment, The B15C5-coated membrane exhibits a sensitive reversible wettability transition property.



Fig. S15 oil contact angles of B15C5-coated mesh after acid/alkaline solution treatment.