# Supporting   Information
## for
## Two-step facile fabrication of superamphiphilic biomimic membrane with micro-nano structure for oil-water emulsion separation on-demand

Qinghong Zeng[a b], Lei Qiu[a b],Siyang Zhao[b] , Jiaxu Zhang[b c], Jinxia Huang*[b], Zhiguang Guo*[a b]


**Affiliations**
*a. Hubei Collaborative Innovation Centre for Advanced Organic Chemical Materials and Ministry of Education Key Laboratory for the Green Preparation and Application of Functional Materials, Hubei University, Wuhan 430062, People's Republic of China.*
*b. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou730000, People's Republic of China*
*c. School of Engineering and Technology, China University of Geosciences, Beijing, People's Republic of China*
Corresponding author:
*E-mail addresses: zguo@licp.cas.cn (Guo) and huangjx@licp.cas.cn (Huang).

## Experimental Section

### Materials.

SSM with 2300 mesh size was obtained from Anping Co., Ltd, Hebei, China. Zinc sulfate，Zinc nitrate，copper sulfate (II) and Ferric chloride were purchased from Chengdu Kelon Chemical (China) Co., Ltd., China. Dopamine hydrochloride (98%) was purchased from Shanghai Macleans Biochemical (China) Co., Ltd. Sodium chloride was purchased from Rainlon (China) Co., Ltd. Phosphoric acid and ammonia purchased from Beijing Chemical works., China. Silicon dioxide nanoparticles ($SiO_2$ NPs) were purchased from Meryer Chemical Technology Co., Span was provided by Tianjin Guangfu Fine Chemical Institute. Sodium laurylsulfonate (AR) was received from Sinopharm Chemical Reagent Co., Ltd. Gasoline was obtained from an adjacent gas station. All other chemical reagents were all of analytical grade and used without further.

### Construction of superamphiphilic biomimic membrane.

Superamphiphilic biomimic membrane was constructed by two-step electrodeposition (Figure 1). For preparation, the SSM, which was cut into a 2.5cm×2.5cm square, was immersed in deionized water and absolute ethanol for 10 minutes to wash off surface dirt. And then, the SSM was put into an etching solution made up of 17ml of deionized water, 3g of ferric chloride, and 3ml of phosphoric acid to react for 2 minutes to remove surface oxides. After that, the SSM was rinsed repeatedly with deionized water, and vacuum-dried. For one-step electrodeposition, the electrodeposition reaction solution was made up of 100ml deionized water ,0.32g zinc Sulfate, 0.16g copper sulfate., 0.123g dopamine hydrochloride and 0.584g sodium chloride. In this electrodeposition reaction, the SSM was used as cathode, and the copper sheet was used as the anode, which shape is 20 mm × 20 mm × 0.1 mm. And the distance between the two electrodes is 2.5cm. For electrodeposition reaction, the voltage is 1.5v for 45min, which achieved the superamphiphilic biomimic membrane (Figure 2). After that, the SBM was rinsed

repeatedly with deionized water, and vacuum dried. After that, it needs to prepare the dip coating solution. Specific steps are as follows: add 0.5g of zinc nitrate to 50ml of ethanol under ultrasonic conditions, and then add 2ml of ammonia water dropwise with stirring. After the liquid is turbid, ultrasonically remove it for 1 hour, add 0.5g of nano-$SiO_2$ and 2%w chitosan turbid solution and stir 30min. After preparing the dip coating solution, the SSM were sequentially immersed in the prepared coating solution for about 1 min, and dry out the SSM, which process was repeated 5 times. The superamphiphilic biomimic membrane with micro-nano structure was prepared.

**Preparation and separation of emulsions**

For this this experiment, the oil-in-water emulsion and water-in-oil emulsion were needs. For oil-in-water emulsion, four oils, which were n-hexane, gasoline, isooctane, and xylene, were mixed with water in a ratio of 1: 100. After adding the AR at a dosage of 0.5 mg/mL, water-in-oil emulsions were formed through stirring and ultrasound. Due to the instability of oil-in-water emulsion, it can only be placed for 24 h. For water-in-oil emulsion, the above four oils were mixed with water in a ratio of 100:1. After adding the Span at a dosage of 1.5 mg/mL, a stable water-in-oil emulsion was formed through stirring and ultrasound. Compared with the oil-in-water emulsion, water-in-oil emulsions can be stored for a long time. For separation of oil -in-water emulsions, the prepared membrane was fixed the above device. And the membrane was need to be wet with oil. In addition, a vacuum pump (Millipore, WP6122050) is required to provide a pressure difference of 2.5 kPa as the driving force (Figure S1a.).

About separation of emulsions, different emulsions were taken different measure. For separation of oil-in-water emulsions, the prepared membrane was fixed in the glass microanalysis filter holder (Millipore) with an effective separation area of 2.27 $cm^2$. And the membrane was need to be wet with water. In addition, a vacuum pump (Millipore, WP6122050) is required to provide a pressure difference of 2.5 kPa as the driving force. For

separation of water-in-oil emulsions, the prepared membrane was fixed the above device. And the membrane was need to be wet with oil. The purity of the separated filtrate was detected by COD. In addition, a vacuum pump (Millipore, WP6122050) is required to provide a pressure difference of 2.5 kPa as the driving force.

**Mechanical stable and anti-fouling test.**

The mechanical stability test is evaluated by sand impact test. The specific steps are as follows: The SSM is placed at the bottom at a certain inclined angle, and 15g of sand falls from a height of 15cm from the SSM (Figure S1b.). The process was repeated 50 times for each 10 times the water contact angle, oil contact angle of water (Dichloroethane), flux and fractional efficiency of the samples were tested.

The anti-fouling test is evaluated by 10 cycles emulsion separation test. During ten cycles, the membrane was tested for flux and separation efficiency. After each separation test, the separation membrane was repeatedly washed with absolute ethanol several times, and then dried.

The chemical stability test is evaluated that PDA/Cu/Zn SSM was soaked in solutions of different pH values for 1h. First, HCl and Na(OH) were prepared in a solution with a concentration gradient from PH=5 to PH=9, and the PDA/Cu/Zn SSM was soaked in it for 1 h, and then the contact angle in the air was taken out to measure the change.

**Separation mechanism**

To understand the separation mechanism of the as-prepared membranes during emulsion separation, the wetting process was modeled assuming that the pores on the membrane surface were distributed in a regular square array. Since the prepared membrane is amphiphilic in air, the contact angle of water and oil droplets on the membrane surface is less than 90° (Figure. S3a) (Figure. S3b). It can be seen from the formula (1) that when the contact angle θ is greater than 90°, the intrusion pressure ΔP is greater than 0. That is, oil and water droplets are blocked without wetting. Therefore, before separating oil-in-water and water-in-oil emulsions, the

prepared membranes must be wetted with the corresponding water/oil. After being wetted by water/oil, a water/oil film will form on the surface of the membrane to transport droplets while blocking the passage of water/oil droplets (Figure. S3c) (Figure. S3d).

Besides wettability, the pore size of the membrane is also important for emulsion separation. Therefore, we performed a second step of dip coating to reduce the pore size. By controlling the pore size to be smaller than the diameter of the emulsified droplets, the above-mentioned superwetting materials can achieve emulsion separation. Because emulsified tiny droplets are intercepted by the membrane surface with smaller pore size (Figure S2e.). Moreover, during the separation process, the filter cake will gradually form on the membrane surface, which can improve the separation efficiency to a certain extent. The droplets that stay in the pores will form a filter cake like a porous membrane, so some emulsions with a particle size smaller than the pore size can also be separated.

$$\Delta P = \frac{2\gamma}{R} = \frac{l\gamma cos\theta}{A} \tag{1}$$

Based on this, the pore size of the membrane is very important for emulsion separation. As shown in Equ (1), the smaller the pore size, the larger the p, which is conducive to the formation of filter cake, so compared with other small mesh SSM, we The maximum mesh size of 2300 was selected. Moreover, selecting other mesh numbers is not because the emulsion cannot be separated, but the effect is not as good as the 2300 mesh selected in this experiment.

**Explain electrodeposition process of PDA/Cu/Zn coating.**

To explain this process, the anodic reactions are shown as Eqs (1)-(5). According to Eqs (1)-(5), first, dopamine is oxidized to dopamine (Eq (1)). Next, dopamine quinone undergoes intramolecular cyclization to form a colorless dopamine pigment (equation (2)) through an addition reaction, which is easily oxidized to dopamine pigment (equation (3)). At this time, the electrolyte turned brown. The dopamine pigment is then further rearranged to form 5,6-

dihydroxyindole, which is further oxidized to 5,6-indolequinone (Eq (4)). Finally, even in acidic electrolyte solutions, 18,19,5,6-indoloquinones are further oxidized to form polymers due to intermolecular crosslinking (Eq (5)). At this point, polydopamine is still present in the electrolyte system. Therefore, the reason for the facile preparation of polydopamine by electrochemical methods is that the anode provides electrons, which proves the reaction energy. On this basis, polydopamine can be electrochemically prepared, and the operation is simple. Afterwards, PDA would attach to the SSM surface, forming a popcorn structure.

Eqs (2)-(6)



(2)



(3)



(4)



(5)



(6)
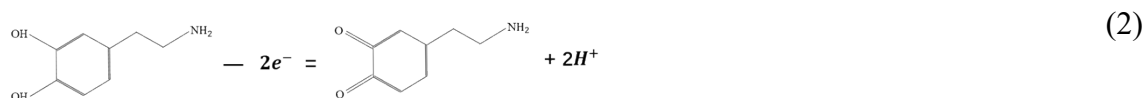
**Original SSM Separation of xylene emulsions.**

To compare the separation effect of our PDA/Cu/Zn SSM, we used the original SSM to perform separation tests under the same conditions on xylene emulsions (including oil-in-water emulsions and water-in-oil emulsions). The water-in-oil emulsion effect and oil-in-water emulsion effect after separation are shown in figure S10. Although it is indeed clearer than the emulsion before separation, the effect is far from that of PDA/Cu/Zn SSM.
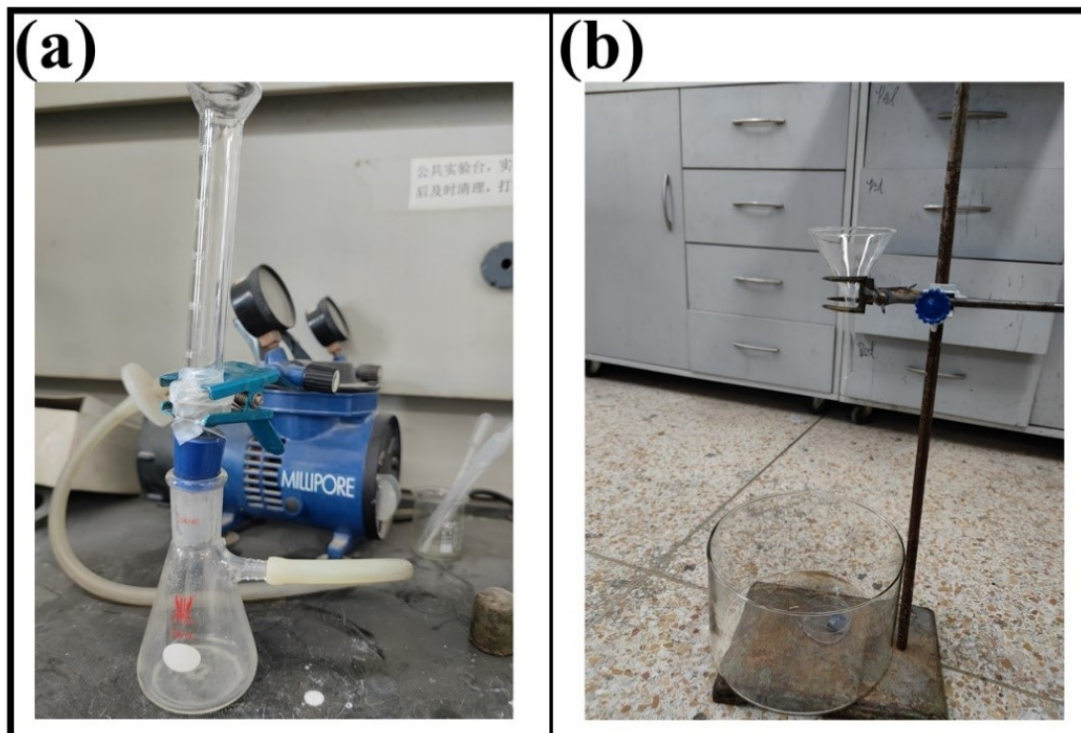
**Figure S1.** (a) Suction filter device. (b) Sand impact device.
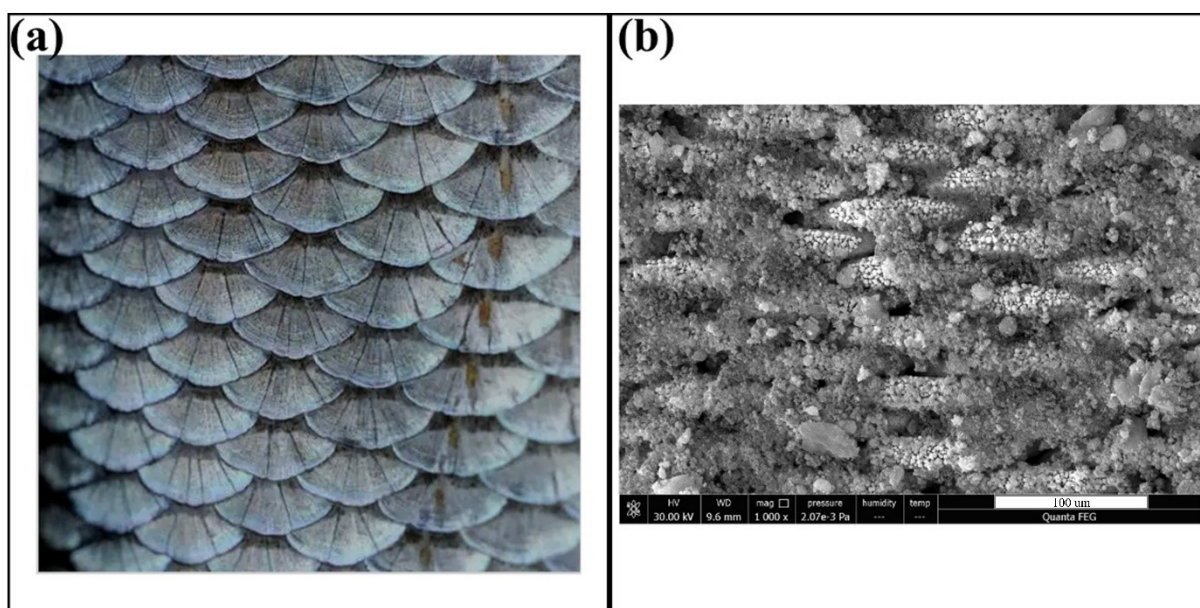


**Figure S2.** Structure comparison of fish scale and PDA/Cu/Zn SSM. (a) fish scale. (b) PDA/Cu/Zn SSM.
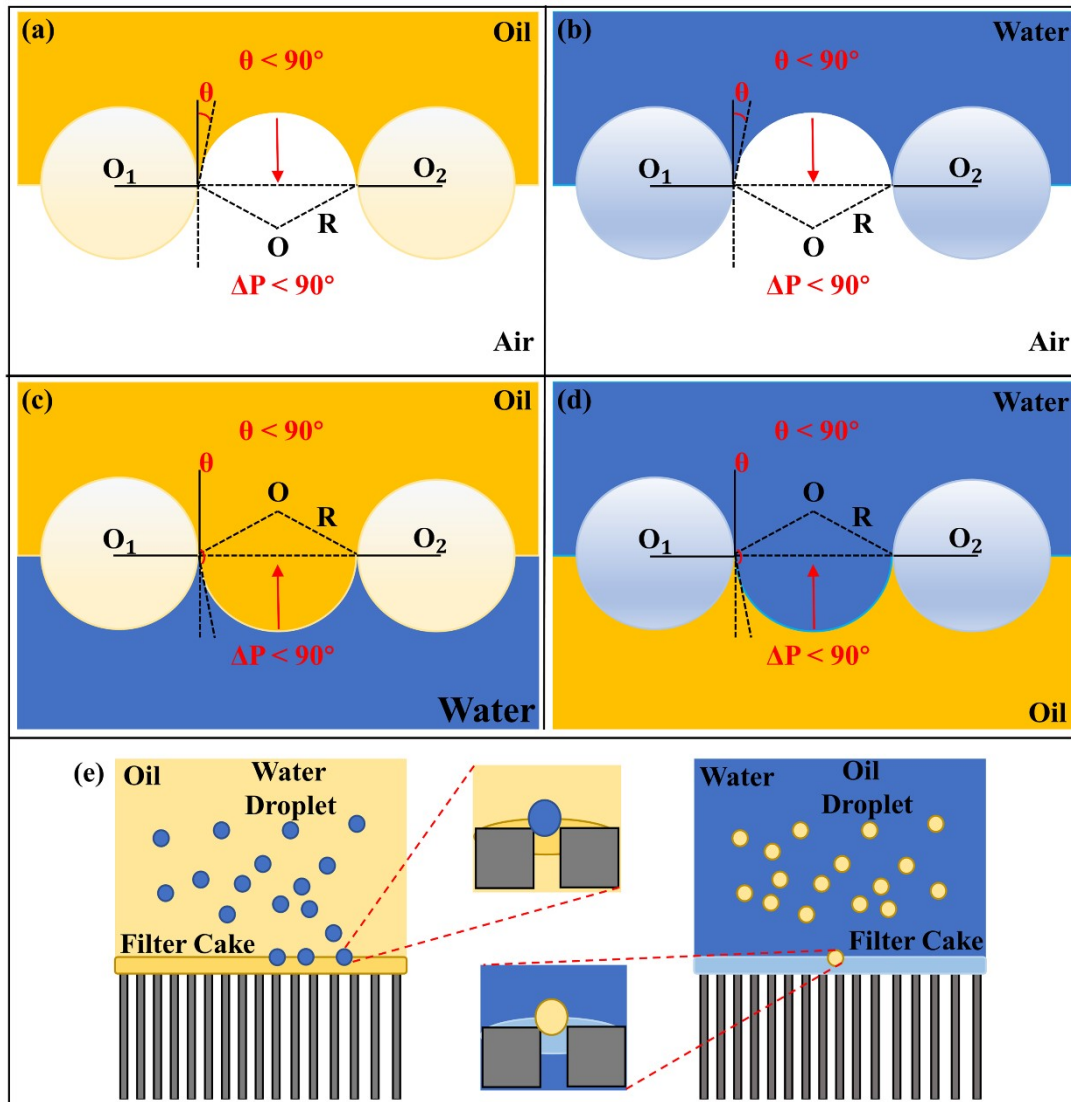
**Figure S3.** Schematic diagram of wetting model for oil-water separation process. (a) and (b) show that oil/water can permeate the membrane, when ΔP is less than 90°. (c) and (d) show that Oil/water is impermeable to underwater superhydrophobic/superoleophobic surfaces that are pre-wetted by water/oil, and thus can block water/oil. And (e) shows that Emulsion separation is through the small pore size of the membrane based on size sieving realized.
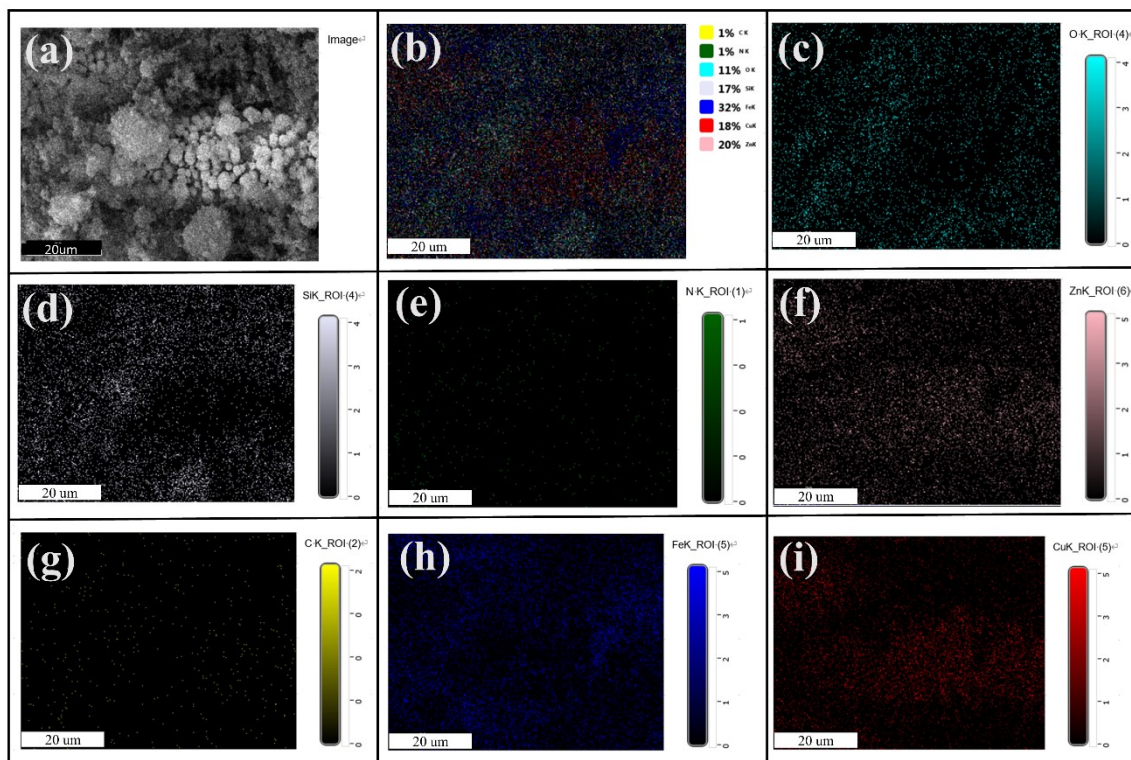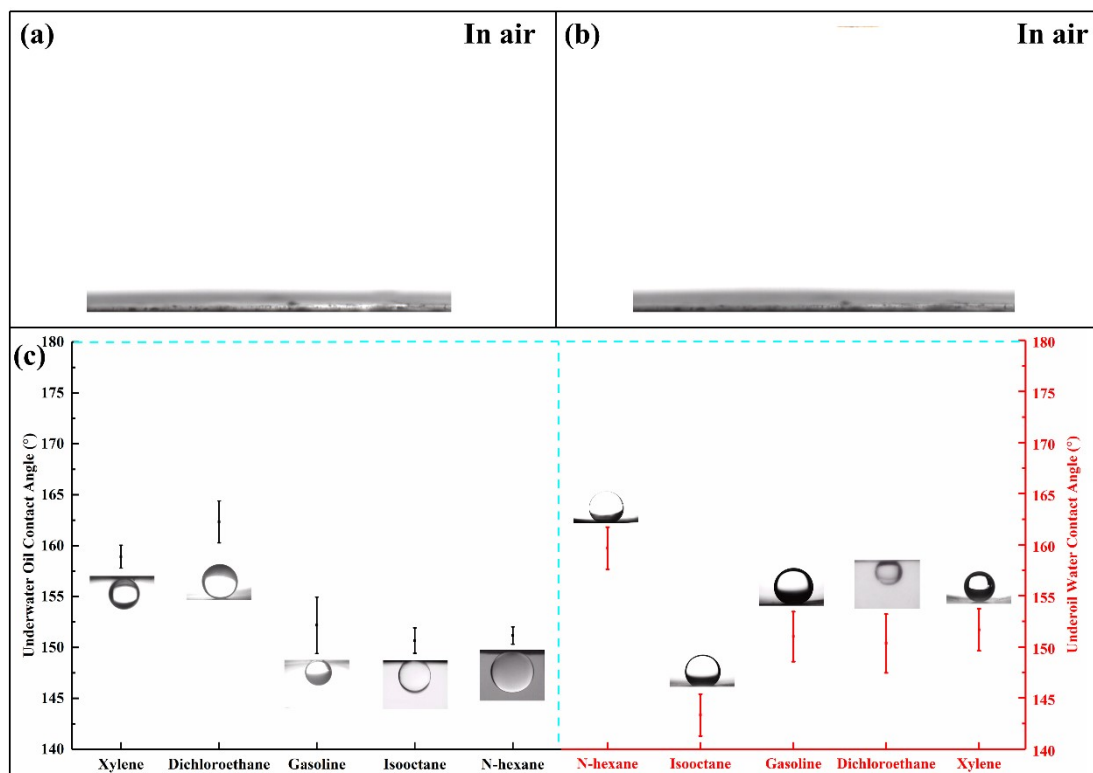
**Figure S4.** The element distribution.
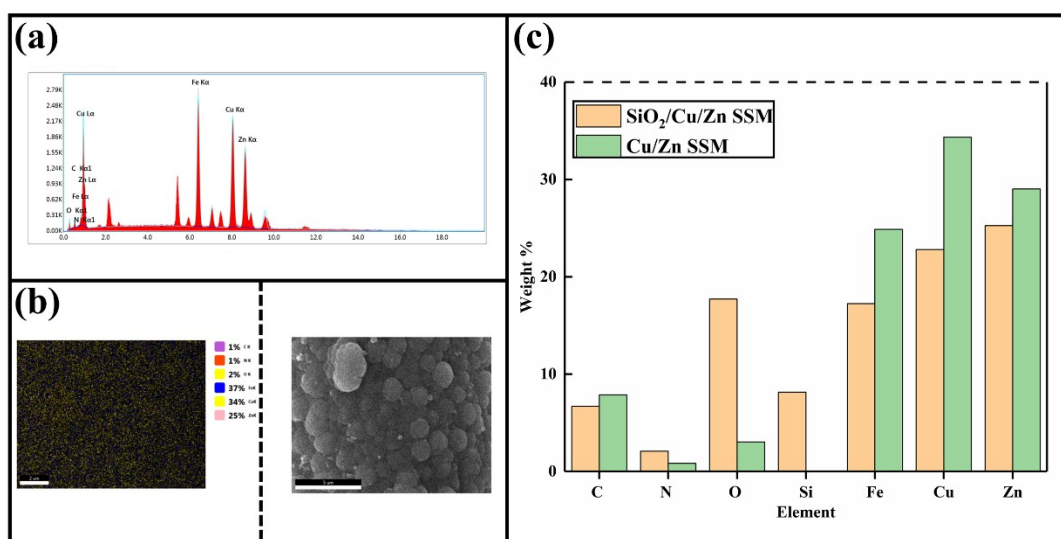


**Figure S5.** (a) The sum spectrum of PDA-Cu-Zn SSM. (b) The element distribution of PDA-Cu-Zn SSM. And (c) the compared elements of coating-PDA/Cu/Zn SSM and PDA/Cu/Zn SSM.

**Figure S6.** (a) the water contact angle of coated-PDA/Cu/Zn SSM in air, (b) the oil contact angle of coated-PDA/Cu/Zn SSM in air and (c) the underwater oil contact angles of coated-PDA/Cu/Zn SSM and underoil water contact angles of SSM.
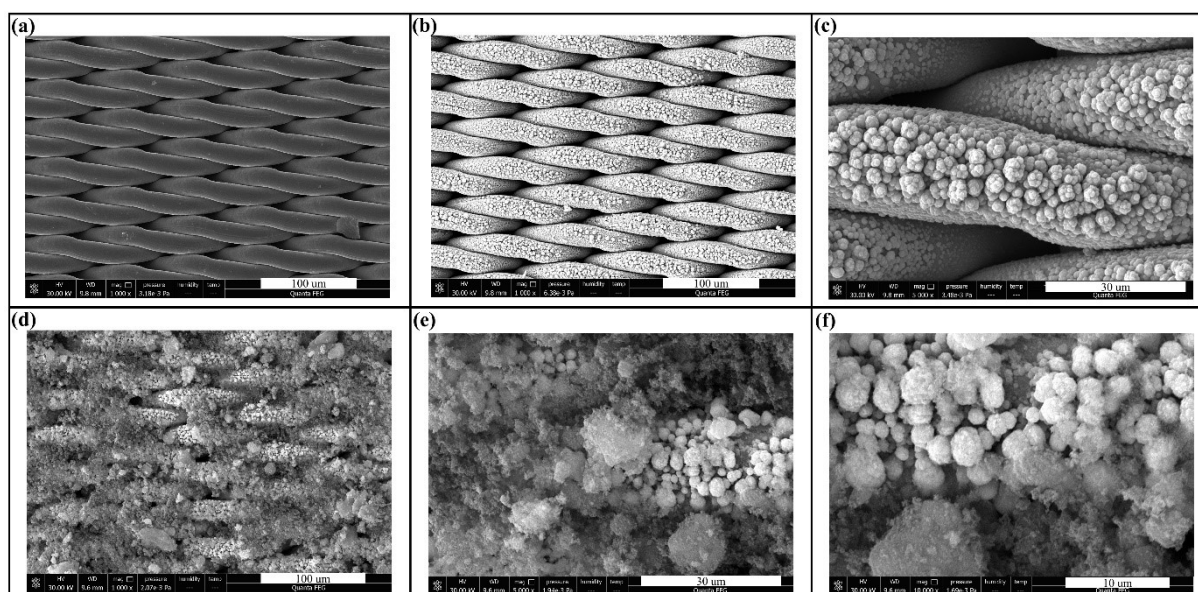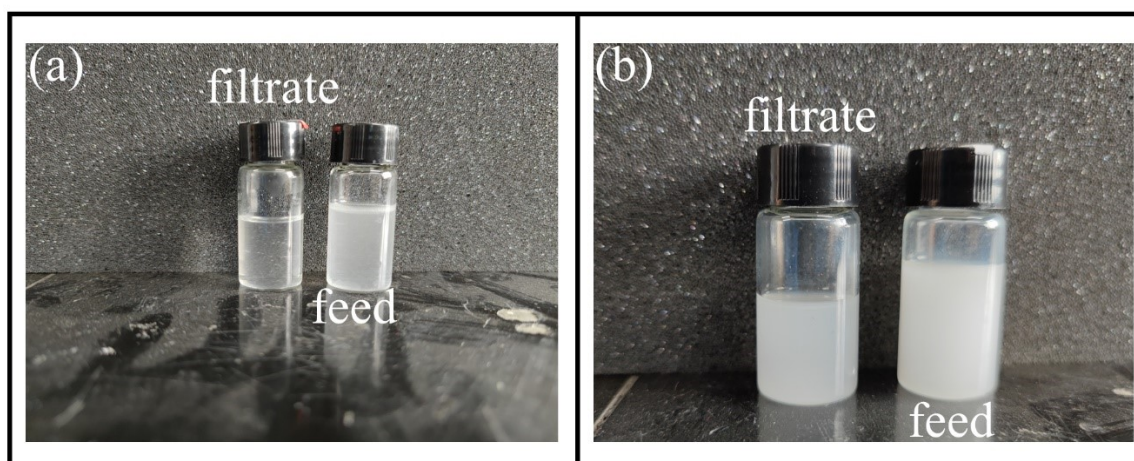
**Figure S7.** (a) original SSM, (b) PDA/Cu/Zn SSM 1000x, (c) PDA/Cu/Zn SSM 5000x, (d) coated-PDA/Cu/Zn SSM 1000x, (e) coated-PDA/Cu/Zn SSM 5000x and (f) coated-PDA/Cu/Zn SSM 10000x.
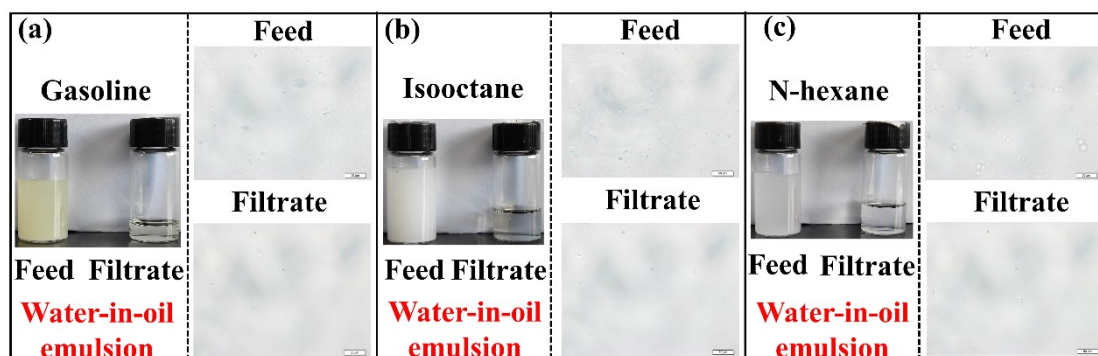


**Figure S8.** The comparison of other three water-in-oil emulsions.
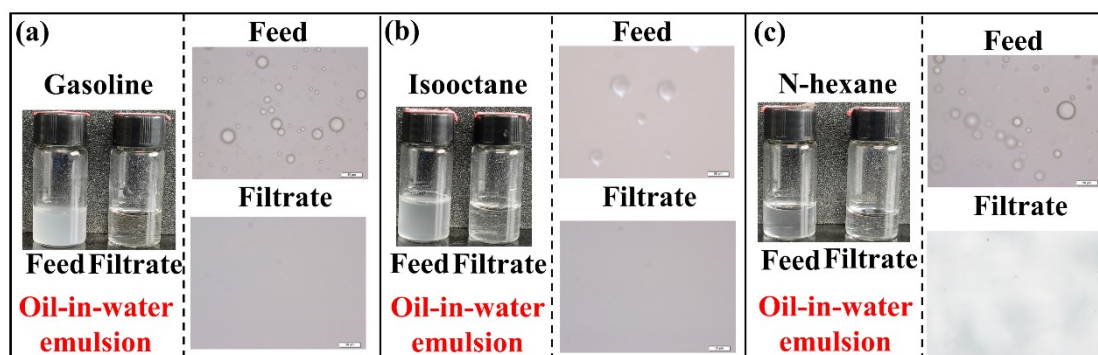


**Figure S9.** The comparison of other three oil-in-water emulsions.



**Figure S10.** The separation effect of original SSM (Xylene emulsion). (a) Xylene oil-in-water emulsion. (b) Xylene water-in-oil emulsion
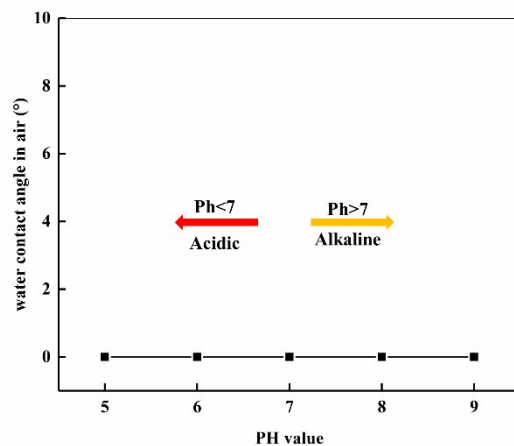
Figure S11. The contact angle of PDA/Cu/Zn SSM after soaking in solutions with different pH values.
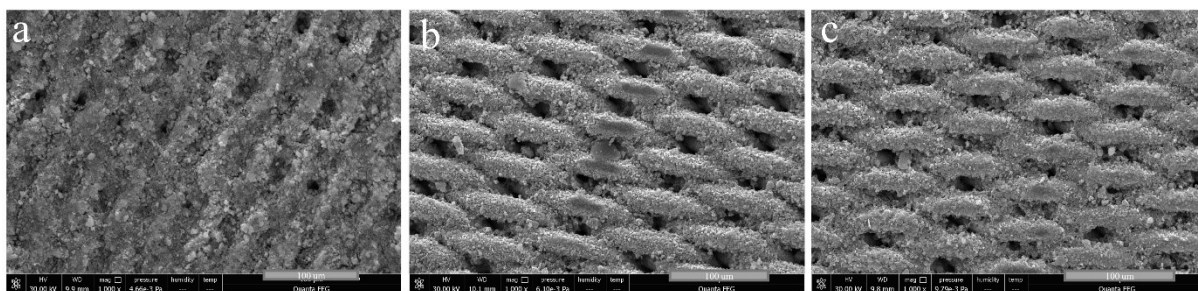


Figure S12. The SEM comparison of DPA/Cu/Zn SSM soaked in pH=7, 5, 9 solution in 2h.

**Supporting information video 1.** Wetting process of oil in air.

**Supporting information video 2.** Wetting process of water in air.

**Table 1**. **The separation performance of our PDA/Cu/Zn SSM compared to other reported membranes**

| Method | Material | Wettability | Water in oil emulsion | Oil in water emulsion | Ref |
|---|---|---|---|---|---|
| Adsorption and filtration approach | PVDF-modified TiO2 nanowires membrane | Under-liquid dual superlyophobicity | >99.3% | >99.3% | [1] |
| Sol–gel and dip-coating methods | TiO2-coated stainless steel mesh | Under-oil superhydrophobicity and underwater oleophobicity | - | - | [2] |
| One-pot reaction | Nanobiofibers | Under-oil superhydrophobicity and underwater superoleophobicity | - | 99.87% | [3] |
| Immersion | TiO2 nanoparticles and dopamine coated PVDF membrane | Superhydrophilicity | - | Nearly 99% | [4] |
| Biomimetic silicification | Silica-decorated polypropylene microfiltration membranes | Superhydrophilicity and underwater superoleophobicity | | Above 99% | [5] |
| Electrodeposition and dip-coating approach | PDA/Cu/Zn | Superamphiphilicity | >99.7% | >99.7% | This work |

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