

## Supporting information

### **Facilely and efficiently constructing anti-oil-fouling zwitterionic coating on membranes for oil-in-water emulsion separation**

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#### **Experimental Section**

**Materials.** The polyvinylidene fluoride membrane (PVDF, mean pore size 0.45  $\mu\text{m}$ ) were purchased from Yibo Filter Equipment Factory (Haining, China). Tannic acid (TA, AR), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA, AR), (3-aminopropyl) triethoxysilane (APTES, AR), iron sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ , AR), N-(3-Sulfopropyl)-N-(methacryloxyethyl)-N, N-dimethylammonium betaine (SBMA, 97%), tris(hydroxymethyl)aminomethane (Tris), and Tween 20 were provided by Aladdin (China). Ammonium persulfate (APS, AR) supplied by Xilong Chemical Co. LTD. Ethanol is by from Tianjin Kermel Chemical Reagent Co., Ltd. (China). Crude oil (viscosity:  $\sim 80\text{mPa}\cdot\text{s}$ ; density:  $\sim 0.8\text{ g/cm}^3$ ) was supplied by China Petro-Chemical Corporation. All chemicals can be used directly without further purification.

#### **Synthesis of $\text{M}_n$ .**

The pristine polyvinylidene fluoride (PVDF) membrane (M) was dipped by ethanol before the first modification. 0.05 g of tannic acid (TA) was dissolved in 25 mL of Tris-HCl buffer solution (pH = 8.5), and then stirred to completely dissolved, and then the PVDF dipped with ethanol was soaked in the TA solution. Subsequently, 5 mL ethanol dissolved with 50  $\mu\text{L}$  of APTES and three different amounts of 3-(trimethoxysilyl) propyl methacrylate (TMSPMA) (25  $\mu\text{L}$ , 50  $\mu\text{L}$ , and 75  $\mu\text{L}$ , respectively) was added into the above solution, and stirred for 12 h. Next, the membrane was

washed with ethanol for several minutes to remove residual solutions. According to the amount of TMSPMA (0  $\mu\text{L/mL}$ , 1  $\mu\text{L/mL}$ , 2  $\mu\text{L/mL}$ , and 3  $\mu\text{L/mL}$ ), the membranes were named as  $M_0$ ,  $M_1$ ,  $M_2$ , and  $M_3$ . The details of the name of membranes and the corresponding modification are showing Table S1.

### **Synthesis of $M_n$ -PSBMA.**

The membranes of  $M_n$  were immersed into the monomer solution (3 mg/mL SBMA, 1 mg/mL  $\text{Fe}^{3+}$  and 3 mg/mL APS) for 45 min to undergo the successive redox-reaction-triggered interface radical polymerization to form the PSBMA on  $M_n$  surface. The resulted membranes were named as  $M_0$ -PSBMA,  $M_1$ -PSBMA,  $M_2$ -PSBMA, and  $M_3$ -PSBMA. The details of the name of membranes and the corresponding modification are showing Table S1.

### **Characterization.**

Surface morphologies and energy-dispersive spectroscopy (EDX) of membranes were measured by scanning electron microscopy (SEM, S-4500, Hitachi, Japan). The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were conducted by Spectrum One instrument (PerkinElmer, USA). Contact angles of different membranes were tested by optical contact angle (MODEL: SL200KB). Oil content was obtained by Total Organic Carbon (TOC) analyzer (O.I. Analytical, USA). The light microscope photographs were measured by optical microscope (BM-60XCC) photograph. Oil droplet size distribution was tested by dynamic light scattering (DLS) measurement (ZetaPlus, Brookhaven Instruments, Holtsville, NY).

### **Emulsion separation performance**

15 mL soybean oil and 0.02 g Tween 20 were added to 85 mL of water, and the mixture was stirred vigorously for 3 h to acquire the oil-in-water emulsion. The light microscope photograph and the oil droplet size distribution of the emulsion were shown in Fig. 4a, and the oil droplets in the emulsion ranges between 0.5  $\mu\text{m}$  to 16  $\mu\text{m}$ . The oil-in-water emulsion separation performances of membranes were carried out by cross-flow mode. The cross-flow flux was 40  $\text{L h}^{-1}$  and the trans-membrane pressure was 0.2 bar. Each separation cycle includes 20 min for separating pure water and 60 min for separating the oil-in-water emulsion. Subsequently, the membrane underwent a simple washing with water. This protocol was repeated for three cycles. The water

flux of membrane was calculated by the following equation:

$$J = V / (A \times t \times P)$$

where  $V$  (L) is the permeate volume,  $A$  ( $\text{m}^2$ ) is the effective area ( $4.5 \times 10^{-4} \text{ m}^2$ ) of membrane,  $t$  (h) is the filtration time, and  $P$  is the operation pressure (0.2 bar).

The antifouling property of the membrane is respectively evaluated by the flux recovery ratio ( $FRR$ ), The  $FRR$  of membrane was calculated by the following equation:

$$FRR = J_{W2} / J_{W1} \times 100\%$$

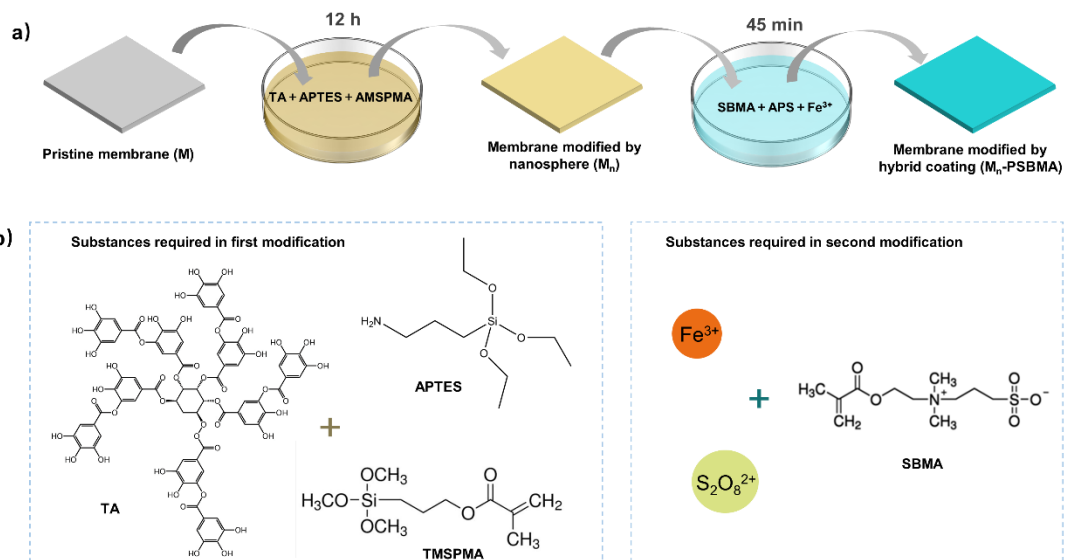
The oil rejection of the filtration process is determined by the following equation:

$$R = (1 - C_p / C_o) \times 100 \%$$

Where  $R$  is the rejection of membrane separating oil-in-water emulsion;  $C_p$  and  $C_o$  represent oil concentrations of filtrate and emulsion, respectively.

#### **Acid and alkali resistance test**

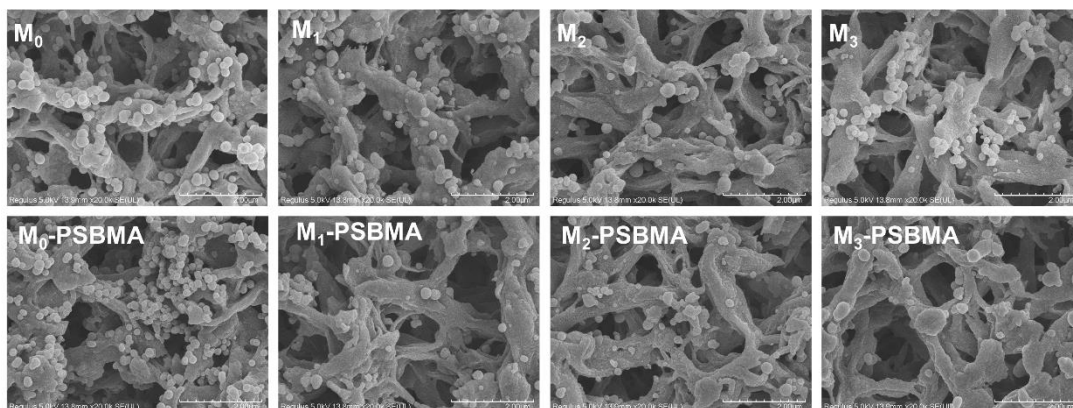
The membrane was immersed in solutions with different pH (pH =2, 3, 5, 7, 9 and 10, respectively) for 12 h, and then the water contact angle and underwater crude oil and soybean oil contact angle of the tested membranes were measured to test the resistance of the membrane to acid and alkaline. The pH of solutions was adjusted by NaOH and HCl.



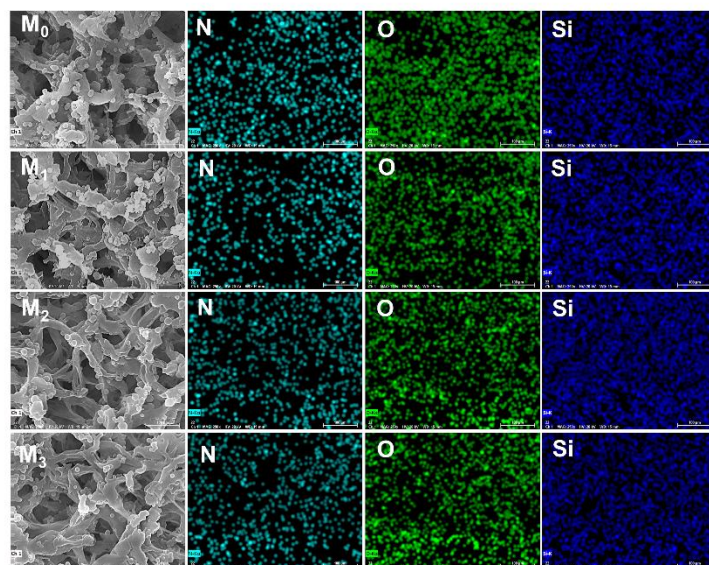
**Fig. S1** (a) The synthesis process of  $M_n$  and  $M_n$ -PSBMA. (b) The materials used and the structure of them.

**Table S1.** The detailed modification conditions of M<sub>n</sub> and M<sub>n</sub>-PSBMA

Membranes	TA (mg/mL)	APTES ( $\mu$ L/mL)	TMSPMA ( $\mu$ L/mL)	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (mg/mL)	APS (mg/mL)	SBMA (mg/mL)
M (PVDF)	\	\	\	\	\	\
M <sub>0</sub>	2	2	0	\	\	\
M <sub>1</sub>	2	2	1	\	\	\
M <sub>2</sub>	2	2	2	\	\	\
M <sub>3</sub>	2	2	3	\	\	\
M <sub>0</sub> -PSBMA	2	2	0	1	3	3
M <sub>1</sub> -PSBMA	2	2	1	1	3	3
M <sub>2</sub> -PSBMA	2	2	2	1	3	3
M <sub>3</sub> -PSBMA	2	2	3	1	3	3



**Fig. S2** The SEM images of the membranes of  $M_n$  and  $M_n$ -PSBMA. The scale bar is 2  $\mu\text{m}$ .

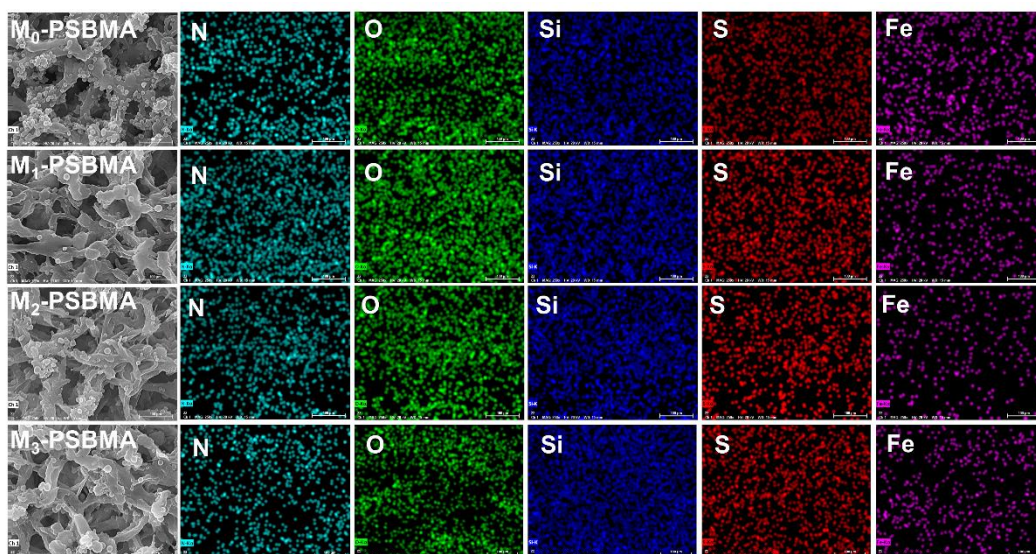


**Fig. S3** The EDX images of M<sub>0</sub>, M<sub>1</sub>, M<sub>2</sub>, and M<sub>3</sub> (The scale bar is 100 μm).

**Table S2.** The element percentages of M<sub>n</sub>.

Membranes	Composition (At. %)		
	N	O	Si
M <sub>0</sub>	24.84	69.32	5.82
M <sub>1</sub>	26.34	65.34	8.31
M <sub>2</sub>	26.53	65.86	7.60
M <sub>3</sub>	30.20	60.10	9.70

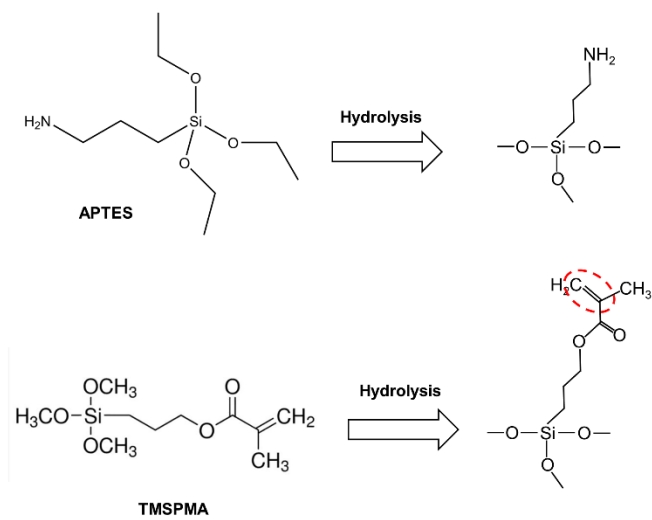




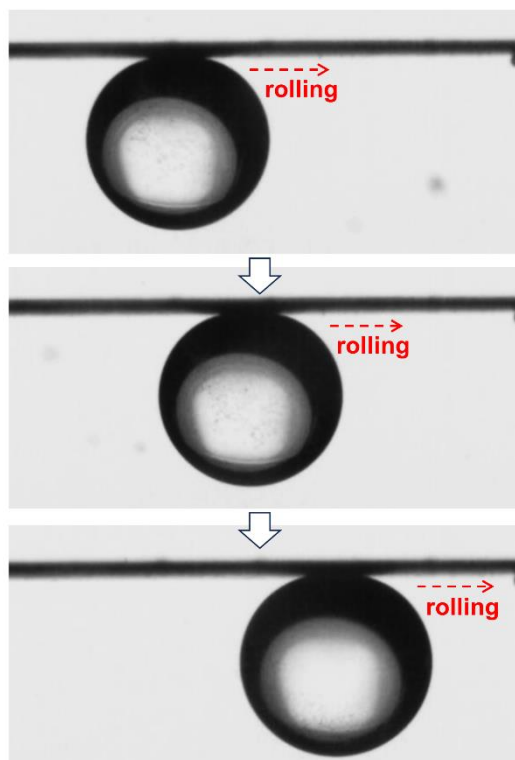
**Fig. S4** The EDX images of M<sub>0</sub>-PSBMA, M<sub>1</sub>-PSBMA, M<sub>2</sub>-PSBMA, and M<sub>3</sub>-PSBMA (The scale bar is 100 μm).

**Table S3.** The element percentages of M<sub>n</sub>-PSBMA.

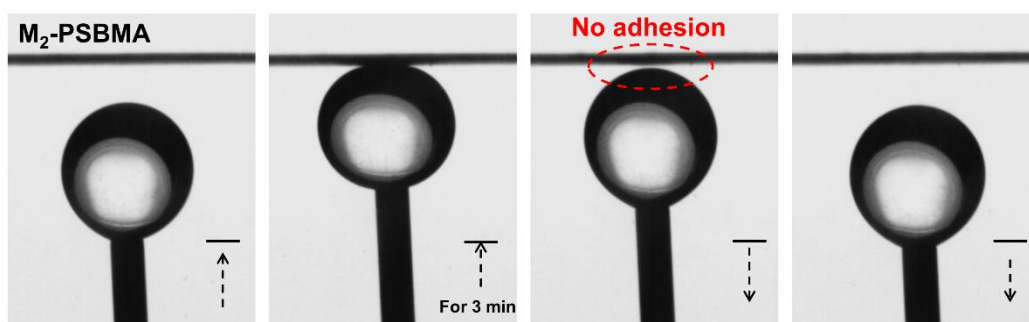
Membranes	Composition (At. %)				
	N	O	Si	S	Fe
M <sub>0</sub> -PSBMA	24.36	67.9	4.69	0.15	2.90
M <sub>1</sub> -PSBMA	31.88	62.18	3.7	1.17	1.08
M <sub>2</sub> -PSBMA	29.66	63.58	4.99	1.33	0.43
M <sub>3</sub> -PSBMA	26.79	60.90	9.81	1.27	1.23



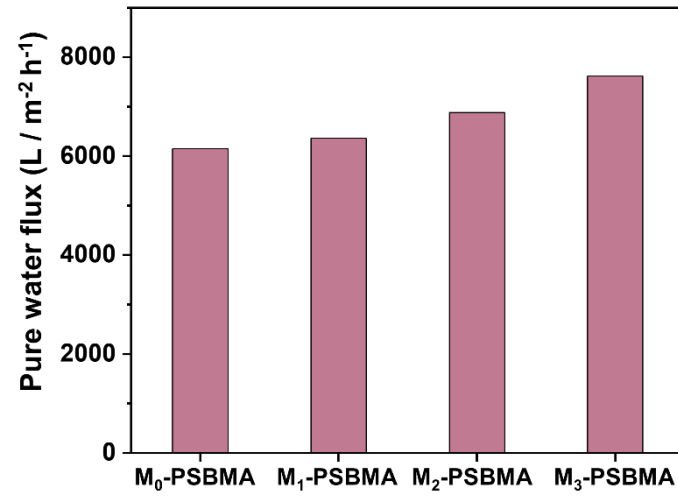
**Fig. S5** The structure of APTES and TMSPMA and the hydrolysate of them.



**Fig. S6** The optical photos of the soybean oil roll-off from the M<sub>2</sub>-PSBMA.



**Fig. S7** The optical photos of the dynamic process to press soybean oil on M<sub>2</sub>-PSBMA for 3 min.



**Fig. S8** The pure water flux of M<sub>0</sub>-PSBMA, M<sub>1</sub>-PSBMA, M<sub>2</sub>-PSBMA, M<sub>3</sub>-PSBMA.

**Table S4** The comparison of M<sub>2</sub>-PSBMA with other published works.

Membranes	Pore size	Duration of continuous filtration	Initial flux (L/m <sup>2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Final flux (L/m <sup>2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Filtration model	Oil rejection	Ref.
SF-DA@PVDF	0.22 μm	30 min	~8000	~4500	cross-flow	>99.1%	<sup>1</sup>
PVDF@MOF-303	0.45 μm	20 min	~3800	~1500	dead-end	> 99.2%	<sup>2</sup>
ZNG-g-PVDF	0.22 μm	120min	~2250	~1250	cross-flow	99.8% (19 ppm)	<sup>3</sup>
PVDF-PG/KH792	0.22 μm	20min	~2950	~2750	dead-end	>99%	<sup>4</sup>
TPS-PVDF	0.22 μm	30min	1194	821	dead-end	>99%	<sup>5</sup>
TiO <sub>2</sub> or SnO <sub>2</sub> coated PVDF	0.22 μm	15min	~800	~200	dead-end	97.11%	<sup>6</sup>
M <sub>n</sub> -PSBMA	0.45 μm	60 min	6500	5800	cross-flow	99.6% (5.98 ppm)	This work

**Reference:**

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