Supporting Information

A robust COF@MXene membrane for ultra-high flux of water-in-oil emulsion separation

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2. Experimental section

2.1 Materials

p-Phenylenediamine (PDA), Acetic acid, 1,3,5-Benzenetricarboxaldehyde (TFB), 1,4-Dioxane, Hydrogen fluoride, and Ti_3AlC_2 were purchased from Shanghai Maclean Biochemical Co. Polyvinylidene fluoride (PVDF) film was purchased from Haiyan New Oriental Plastic Chemical Technology Co. Ethanol, n-hexane, methylbenzene, cyclohexane, heptane, dichloromethane (DCM), trichloromethane and span 80 were provided from Shuangshuang Chemical Co. (Yantai, China). Gasoline was purchased from petrol stations. All reagents were used without further purification.

2.2 Preparation of MXene

1 g Ti_3AlC_2 was added to 20 mL Hydrogen fluoride and stirred at a constant temperature of 30°C for 24 h. After etching, the obtained $Ti3C_2T_x$ (MXene) was washed by repeated centrifugation with a large amount of deionized water until the solution pH was > 6. The solution was dried in a vacuum drying oven. Then the obtained black powders were dried in a vacuum drying oven at 60°C.

2.3 Preparation of superhydrophobic COF@MXene membrane

100 mg MXene, 40 mg TFB, 40 mg PDA, 200 μL Acetic acid, and 30 mL 1,4-Dioxane were mixed together. The mixed solution was stirred at room temperature and pressure for 1-5 days. According to the change of wettability, two days was the optimum reaction time (Figure S1). The products were washed twice with dioxane and alcohol, and then the dried products were denoted as COF@MXene.

A homogeneous suspension was prepared by dispersing COF@MXene particles into absolute ethyl alcohol with the help of ultra-sonication. Subsequently, the superhydrophobic COF@MXene membrane was obtained by depositing COF@MXene particles onto PVDF membrane (1.2 μm) by vacuum filtration. The resulting COF@MXene membrane was dried at 60°C.

2.4 Process of emulsion separation

The single-component water-in-oil emulsions were prepared by mixing water and oil (n-hexane, petroleum ether, dichloromethane, and dichloroethane) in the volume ratio of 1:100 under vigorous stirring for 4 h, Span-80 was added at a ratio of 0.2 g per 100 ml of the emulsion. For complex composition water-in-oil emulsions, 1 mL water corresponds to 99 mL of different oils (10 mL n-hexane, 20 mL methylbenzene, 10 mL cyclohexane, 10 mL gasoline, 20 mL DCM, 20 mL trichloromethane), Span-80 was added at a ratio of 0.2 g per 100 ml of the emulsion. The emulsions separation process was carried out at 0.03 MPa. The permeation flux can be calculated by the following equation I:

$$J_g = \frac{V}{A \times \Delta t} \# \text{ I}$$

$$J_e = \frac{V}{A \times \Delta t \times P} \# \text{ II}$$

Where J_g ($Lm^{-2}h^{-1}$) and J_e ($Lm^{-2}h^{-1}bar^{-1}$) are the permeate fluxes under gravity-driven and external pressure-driven, respectively. V (L) is the volume of permeate in time Δt (h), and A is the effective separation area. P is the external pressure of 0.03 MPa.

The separation efficiency (η) of the membrane was calculated according to the below equation II,

$$\eta = \frac{C_1 - C_2}{C_2} \times 100\% \# \text{III}$$

where C_1 is the feed emulsion concentration, C_2 is the filtrate concentration.

2.5 Characterization

Scanning electron microscopy (SEM, Apreo S) was performed to observe the surface morphologies of Ti_3AlC_2, $Ti_3C_2T_x$, and COF@MXene. The elements in COF@MXene were analyzed using energy-dispersive X-ray spectroscopy (EDS). The chemical compositions of the samples were characterized by Fourier-transform infrared spectroscopy (ATR-FTIR, Bruker, Tensor 27) and X-ray photoelectron spectroscopy (XPS, Kartos AXIS Ultra DLD with Al Kα X-ray Source, HV = 1486.6 eV). The contact angles of water and oil were measured and observed by a goniometer (jgw-360b) with a 5 μL water/oil drop. Thermogravimetric (TGA) analysis was performed to determine the thermal properties of the samples (NETZSCH STA 449F3, 10.0°C/min, 20°C–800°C, air atmosphere). The X-ray diffraction (XRD, Philip X'Pert pro Diffractometer, with Cu Kα X-ray source, λ = 1.54056 Å) was obtained at room temperature. All the optical images were captured using a mobile phone.

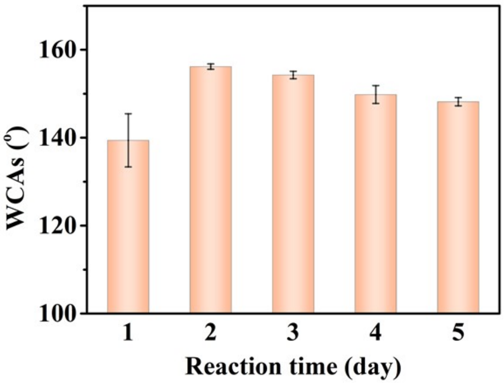

Figure S1. Wettability of COF@MXene under different reaction time.

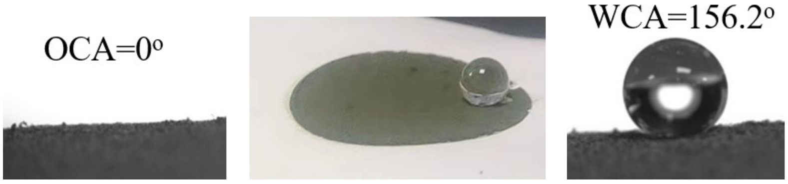

Figure S2. The wettability of COF@MXene membrane.

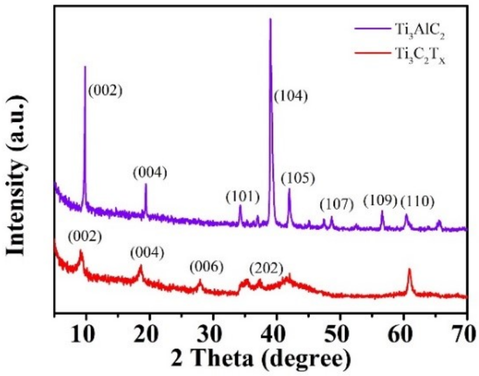

Figure S3. The XRD graph of Ti_3AlC_2 and $Ti_3C_2T_x$-MXene.

According to the XRD pattern of pure MXene, the (002) peak was located at about 2θ=9.42°, and the layer-to-layer spacing calculated by the Bragg equation is approximately 0.94 nm.

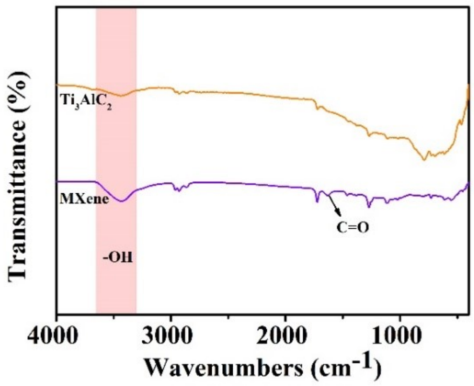

Figure S4. The FTIR graph of Ti_3AlC_2 and MXene.

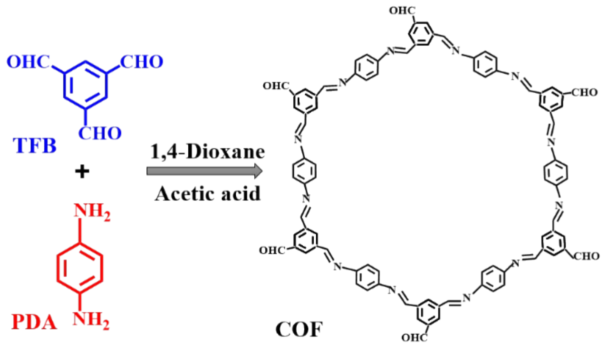

Figure S5. Synthesis process of COF.

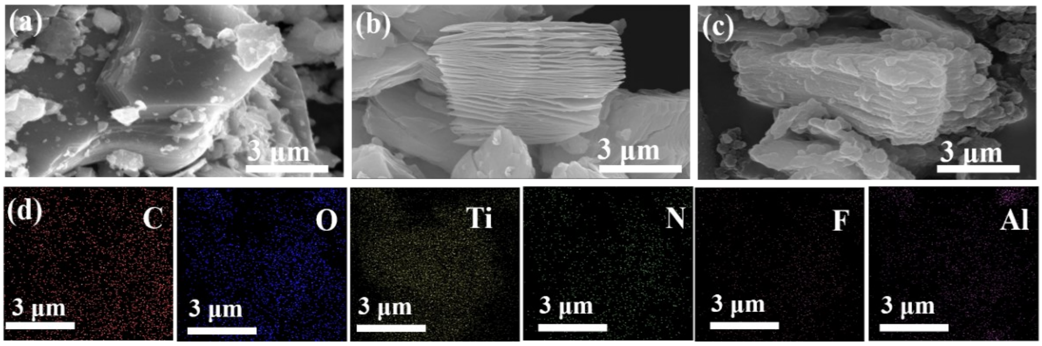

Figure S6. (a)-(c) SEM images of Ti_3AlC_2, MXene, and COF@MXene. (d) EDS pattern of COF@MXene.

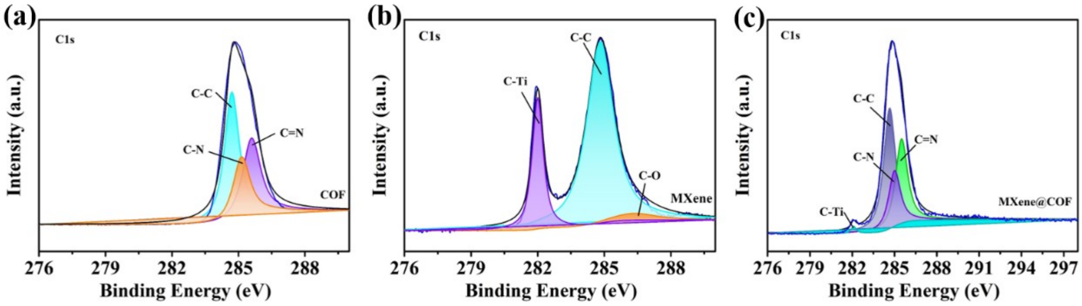

Figure S7. C1s XPS patterns of (a) MXene, (b) COF, and (c) COF@MXene.

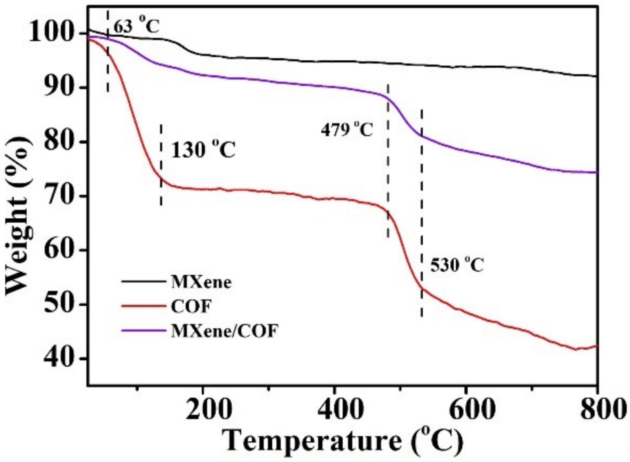

Figure S8. TGA results of COF, MXene, and COF@MXene.

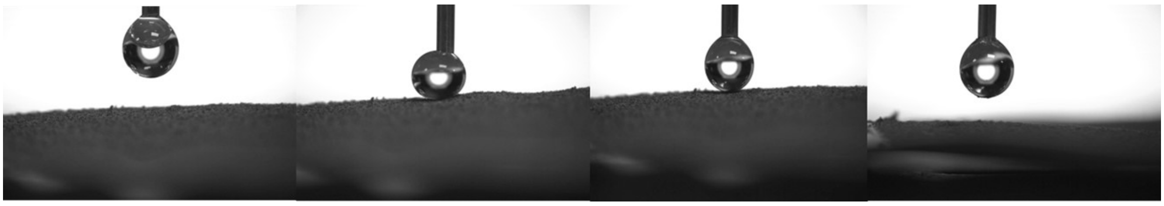

Figure S9. Dynamic contact process of a water droplet on the membrane surface.

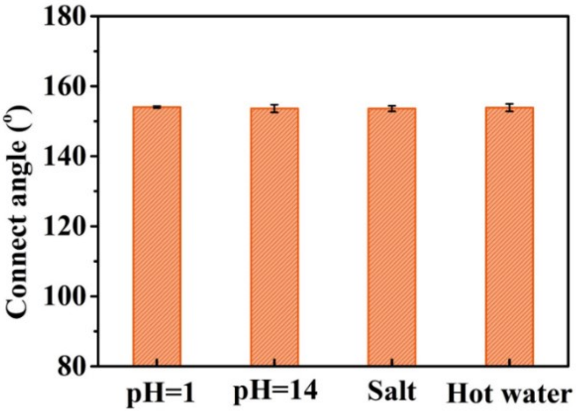

Figure S10. Variation in the water contact angles (WCAs) on COF@MXene with different chemical environments.

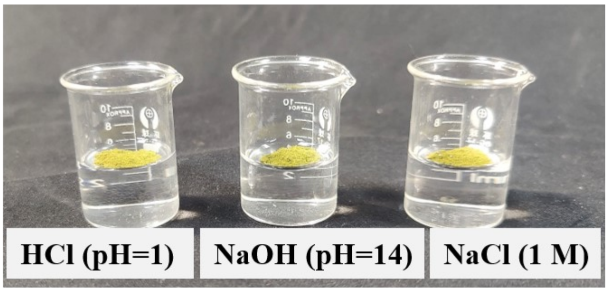

Figure S11. The COF@MXene powders were immersed in different chemical solutions.

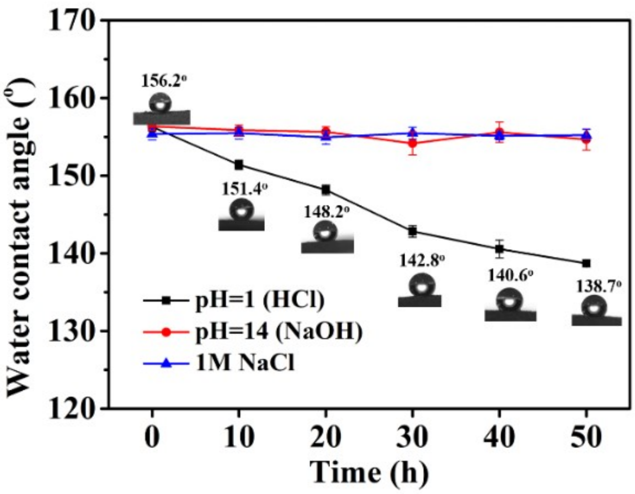

Figure S12. Variation of the WCAs of COF@MXene membrane at different immersion times.

The WCAs of water droplets with different chemical environments were greater than 150°. However, COF@MXene powders were immersed in acidic, alkaline, and salt solutions for 50 h, The COF@MXene powders were filtered into a membrane every ten hours and then tested for their WCAs. As can be seen in Figures S11 and S12, acidic solution destroyed hydrophobic structures, while other chemical solutions maintained stable superhydrophobicity.

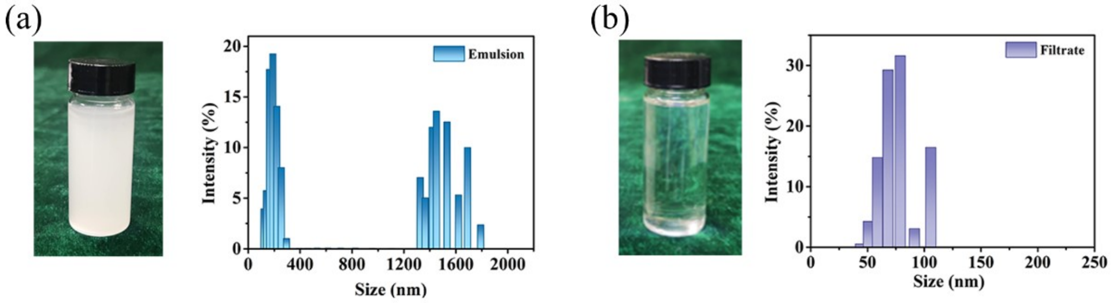

Figure S13. Droplet size distribution (a) before and (b) after COF@MXene membrane separation under external pressure drive.

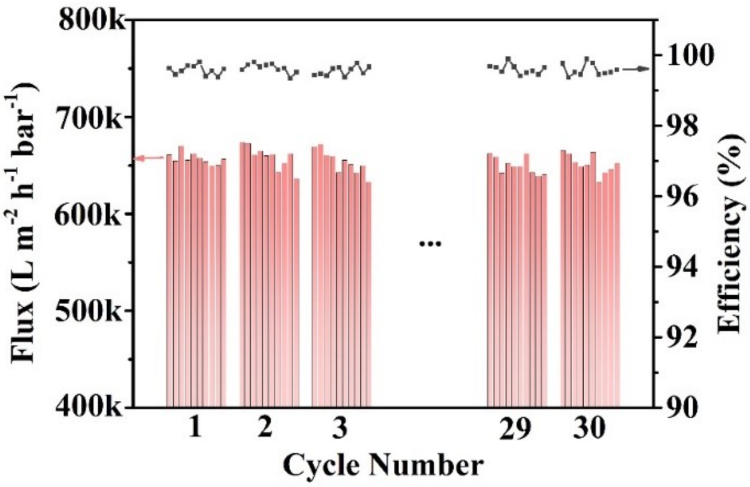

Figure S14. Cyclic adsorption characteristics of COF@MXene membrane for mixed water-in-oil emulsions under external pressure drive.

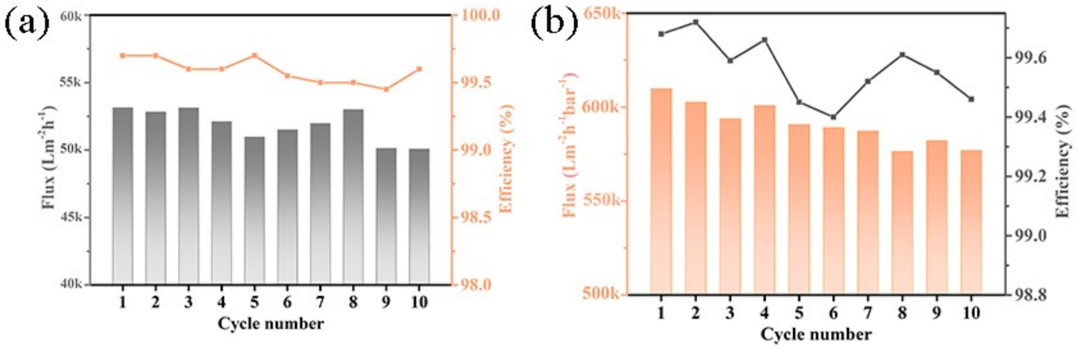

Figure S15. Separation performance of COF@MXene membrane for water-in-trichloromethane emulsion under gravity-driven and external pressure drive.

Table S1. Comparison of different COFs and MXene materials for oily water treatment.

	Material	Mixtures seapration Flux		Emulsions separation Flux		Reference
1	Print paper-based MXene	-	-	Hexane-in-water	682.3 $Lm^{-2}h^{-1}bar^{-1}$	1
2	MXene@UIO-66-$(COOH)_2$	-	-	Multi-component pollutant oil-in-water	713.37 $Lm^{-2}h^{-1}bar^{-1}$	2
3	RGO/PDA/MXene	-	-	Water-in-mixing oil	174.16 $Lm^{-2}h^{-1}bar^{-1}$	3
4	Ultrathin 2D Ti3C2Tx MXene membrane	-	-	Crude oil-in-water	887 $Lm^{-2}h^{-1}bar^{-1}$	4
5	Ultra-thin 2D titanium carbide MXene membrane	-	-	Toluene-in-water	540 $Lm^{-2}h^{-1}bar^{-1}$	5
6	CE-MXene-OH membrane	-	-	Toluene-in-water	6385.93 $Lm^{-2}h^{-1}bar^{-1}$	6
7	COF/GO_{50} coatings	water/ dichloromethane	26,000 $Lm^{-2}h^{-1}bar^{-1}$	-	-	7
8	SSN-supported BTADHBD@Glc@POTS coating	Organic solvents/water	>70 $Lm^{-2}\cdot s^{-1}$	-	-	8
9	PAN/COF	oil/water	4229.29 $Lm^{-2}h^{-1}$	Toluene-in-water	1100 $Lm^{-2}h^{-1}$	9
				water -in-Toluene	1000 $Lm^{-2}h^{-1}$	
10	COF-coated fabric	-	-	water-in-isooctane	18 000 $Lm^{-2}h^{-1}$	10
11	COF@MXene	-	-	water-in-trichloromethane emulsion	643200 $Lm^{-2}h^{-1}bar^{-1}$	This work

- Not reported

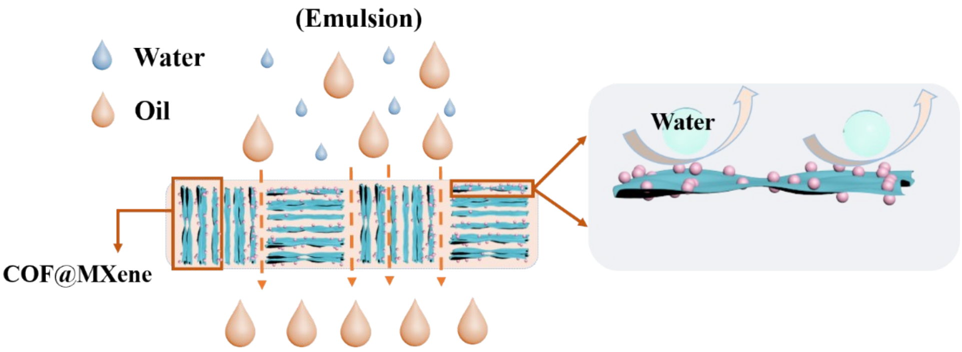

Figure S16. Schematic of the separation mechanism of COF@MXene membrane.

when water-in-oil emulsion contacted COF@MXene membrane, the oil phase could penetrate quickly due to its superlipophilic property. However, the size of trace water in emulsion was repelled to the membrane surface due to the superhydrophobicity. Then the trace water accumulated on the membrane surface and gradually collected into larger droplets, achieving an efficient demulsification process.

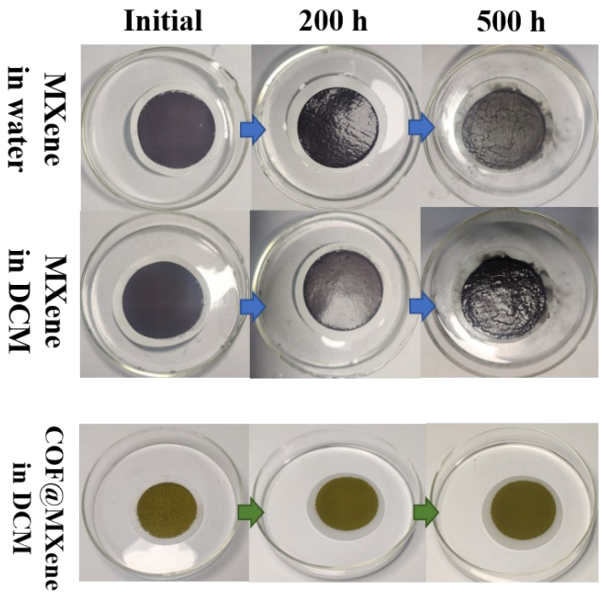

Figure S17. Photographs of the MXene and COF@MXene membrane before and after being immersed in water and dichloromethane (DCM) for 500 h.

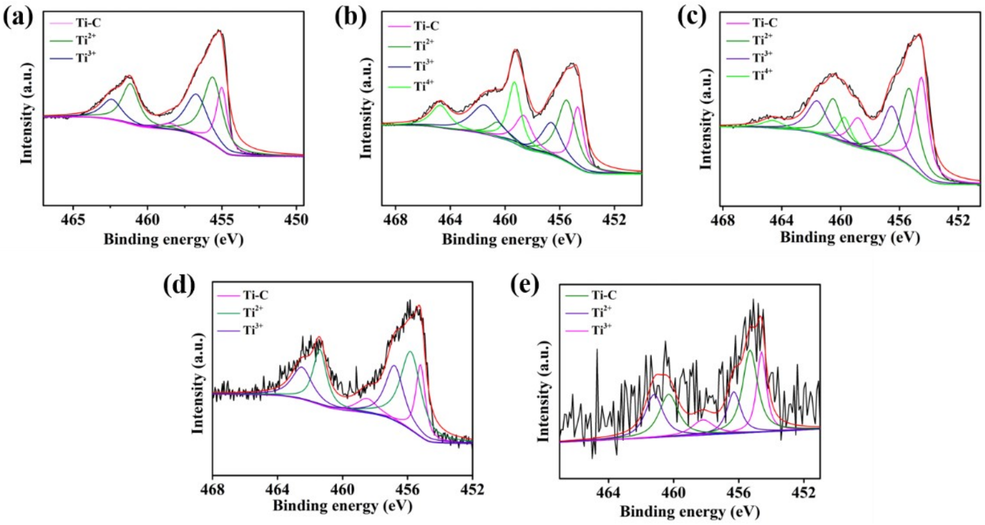

Figure S18. (a) Ti2p XPS of original MXene. Ti2p XPS of MXEne after immersion in (b) water and (c) DCM for 500h. Ti2p XPS of COF@MXEne (d) before and (e) after immersion for 500 h.

When compared to the original MXene, the peak intensity of Ti^{2+} and Ti^{3+} decreased and Ti irons transformed from low chemical valence into high chemical valence (Ti^{4+}) after immersion, which was attributed to the oxidation of MXene[11-13]. It is obvious that the oxidation of MXene is more serious after soaking in water. However, COF@MXene immersed in DCM for 500 h did not show significant oxidation.

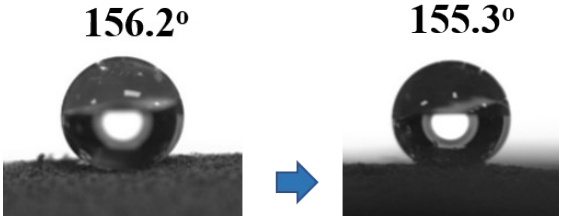

Figure S19. Wettability changes of COF@MXene membrane before and after immersion in DCM for 500 h.

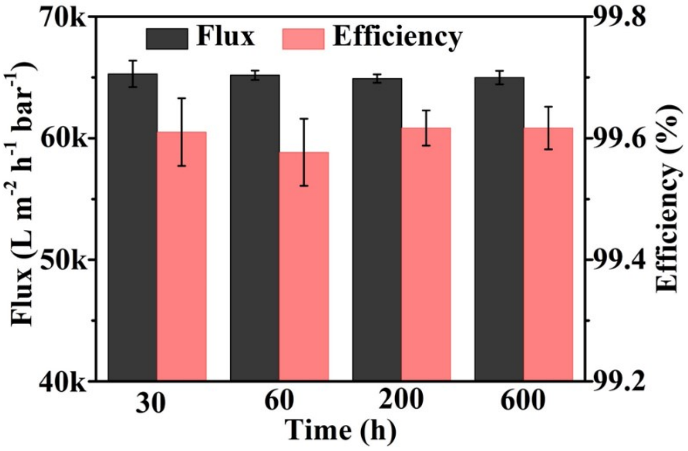

Figure S20. Separation performance of COF@MXene membrane soaked 500 h for separation of water-in-trichloromethane emulsion.

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