Carboxymethyl cellulose and cross-linking with polyethyleneimine to enhance hydrophilicity and antifouling property of polytetrafluoroethylene flat membrane

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ABSTRACT

To enhance hydrophilicity and anti-fouling property of polytetrafluoroethylene (PTFE) flat membrane, a novel and facile method that polyethyleneimine was cross-linked with carboxymethyl cellulose using glutaraldehyde was developed to modify the membrane. The surface morphology, chemical composition, hydrophilicity and anti-fouling property of the PTFE flat membrane were analyzed by attenuated total reflectance Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, water contact angle and pure water flux measurements. Furthermore, the composite membrane could be used for the separation of oil/water emulsion with an ultrahigh efficiency and shows satisfactory oil resistance and antifouling performance. Finally, the composite membrane shows an excellent stability after a long-term separation process, which exhibits potential application in environmental protection.

Keywords: Polytetrafluoroethylene flat membrane; Carboxymethyl cellulose; Hydrophilicity; Anti-fouling property; Oil/water separation

1. Introduction

The ecological environment and health of humans are seriously threatened by oil leakage, untreated industrial oily wastewater, and urban sewage [1–4]. Membrane separation technology is a popular research topic in the field of separation of oil–water mixtures. Relative to conventional technologies, membrane separation technology responds more efficiently to the requirements of process intensification strategy due to its excellent separation selectivity and permeability, low energy consumption, environment-friendly, and easy operation [5,6]. At present, effective oil–water separation could be achieved by utilizing the surface wetting property changes of solid surface [7,8]. There are two types of oil–water separation materials, based on the different wetting properties, "oil-removing" type materials with super-hydrophobicity and "water-removing" type materials with super-hydrophilicity [9]. The superhydrophobic materials are easily contaminated by oil due to their oleophilicity, while the superhydrophilic

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materials are oleophobic [10,11]. The prominent features of the polytetrafluoroethylene (PTFE) flat microfiltration membranes, such as suitable pore size, high porosity, environmental sustainability, excellent chemical resistance, and high mechanical strength [12,13], expand the application in membrane separation technology. However, the PTFE membrane has a low surface energy, its strong hydrophobicity limits practical applications in water treatment [14]. Therefore, hydrophilic modification of PTFE flat microfiltration membrane has great practical significance for improving the anti-fouling performance, expanding the range of applications, and prolonging the service life of membrane materials [15,16].

In the past decades, various approaches have been adopted to endow membranes with excellent hydrophilicity, anti-fouling property, and stability. According to previous studies, hydrophilic modification methods are divided into two categories. One way was by surface modification after breaking the C–F bond, such as wet-chemical method [17–19], plasma treatment [20–22], and irradiation [23,24]. The other way was the direct surface coating technology [25,26]. However, both methods have some disadvantages and limitations. For example, plasma treatment and irradiation technology are high cost, which limits its industrial application. Compared with the above techniques, surface coating modification is more easily achieved. Unfortunately, the physical adsorption capacity of the hydrophilic coating formed is weak. Therefore, a simple and efficient hydrophilic modification methods are urgently needed.

In our previous studies [27], to enhance the hydrophilicity and anti-fouling property of PTFE flat membrane, the PTFE flat membrane was modified via cross-linking o-carboxymethyl chitosan (OCMCS) and polyethyleneimine (PEI) with glutaraldehyde (GA). However, the modified membrane not only has insufficient surface hydrophilicity water contact angle (WCA = 69° ± 3°) and is difficult to be used for oil–water emulsion separation, but also the self-cleaning properties of modification membrane were not considered, it is necessary to select substances with stronger bonding ability with water to modify the membrane. Carboxymethyl cellulose (CMC) possesses large numbers of hydrophilic groups (i.e., –COONa, COOH and –OH), can be used as a hydrophilic agent in the hydrophilic modification of PTFE membrane. CMC is an anionic, water-soluble cellulose ether obtained by chemical modification the natural cellulose [28,29]. At the molecular level, the structure of CMC is quite like cellulose, still retains the structural unit of β-glucose possessed by cellulose, and has outstanding hydrophilic properties and water binding ability. The major difference between CMC and cellulose is that the hydrogen atoms from some hydroxyl groups present in the original cellulose are replaced by carboxymethyl substituent (–CH$_2$COO$^-$) [30]. Compared with natural cellulose, CMC has better water solubility properties and higher chemical reactivity, and can cross-link with epichlorohydrin [31] and glutaraldehyde [32–34] to form stable crosslinked network.

Herein, based on the existed modification methods, a simple approach called as post-crosslinking modification method was studied. First, CMC and PEI as hydrophilic agent were utilized and PTFE membrane was immersed in CMC/PEI solution. Second, glutaraldehyde (GA) applied as cross-linking agent was dropped into the solution and PTFE-CMC/PEI-GA membrane was synthesized. The relationship between reaction conditions and hydrophilicity of the modified PTFE flat membrane was studied.

2. Experimental

2.1. Materials and reagents

Polytetrafluoroethylene (PTFE) flat membrane is supplied by Zhejiang Kertice Hi-Tech Fluor-material Co., Ltd., China. Carboxymethyl cellulose (CMC) and polyethyleneimine (PEI, M_w = 1,800) is purchased from Shanghai Aladdin Chemicals Co., Ltd., China. Glutaraldehyde (GA, 25 wt.%), ethanol, Tween-20, hydrochloric acid, and acetone were supplied from by Hangzhou Gaojing Fine Chemicals Co., Ltd., China. All PTFE flat membrane samples were washed by acetone before using and all reagents used without further purification.

2.2. Modification of the PTFE flat membrane

PTFE flat membranes were first immersed in acetone for 1~1.5 h and subsequently cleaning with acetone to remove surface impurities and contamination. After that, they were dried at 50°C for a few minutes in the vacuum oven. CMC and PEI were dissolved in deionized water at 25°C, the CMC concentration is 0, 2.5, 5, 10 and 20 g L^{-1}, respectively, the CMC and PEI mass ratio is 4:0, 4:1, 3:1, 2:1 and 1:1, respectively. PTFE flat membrane was immersed in the freshly prepared solution after pre-wetting with ethanol, and then added to 2 mL GA solution (0, 3, 5, 7, and 9 g L^{-1}), the reaction was stirred for a designated time at 25°C. The modified membranes were rinsed with deionized water and dried in a vacuum chamber at 50°C. The CMC/PEI modified membranes were named as PTFE-CMC/PEI-GA membranes in this paper.

2.3. Characterization of the PTFE flat membrane

The surface properties of membrane, including surface chemical composition, surface morphology and wettability were measured by X-ray photoelectron spectroscopy (XPS, Kratos, XSAM 800, US) [35], attenuated total reflectance Fourier-transform infrared (ATR-FTIR, Nicolet 5700, America) [36], field-emission scanning electron microscopy (FESEM, Vltra55, ZEISS) and static water contact angle goniometer (WCA, JY82B, China), respectively. The droplet size of the oil/water emulsion was tested by dynamic light scattering (DLS) laser particle size analyzer (Mastersizer 2000, UK). The concentration of the oil/water emulsion was tested by UV-vis spectrometer (752N, China), and the oil rejection was calculated by Eq. (1) [37,38]:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad (1)$$

where C_p and C_f are the concentration of oil after and before filtration, respectively.

2.4. Tests of surface hydrophilicity and separating property of oil/water emulsion

The pure water flux determination was performed in the pressure-driven filtration mode using a homemade cross-flow filtration system (Fig. 1) where the different PTFE membranes were loaded in the filtration cells (effective membrane area: 13.84 cm^2). Before taking samples for analysis, the prepared membranes were compacted at 0.2 MPa for 30 min to reach a stable value, and then the pure water flux was measured at 0.1 MPa. The water flux was measured for all membranes at the same pressure and each reported value is the average of three samples.

In order to carry out oil/water separation and anti-fouling test of the modified membranes, the oil/water emulsion was prepared as follows: 1 g of vegetable oil was added to 1,000 g deionized water with 0.1 g of Tween-20 was used as the emulsifier, and then the mixture was stirred at 10,000 rpm for 1 h. Then, the tests were conducted under the pressure of 0.05 MPa. The anti-fouling performance was evaluated by a three cycle filtration processes. After each cycle, the tested membrane was removed and cleaned by water for 30 min. The water flux of the membrane was calculated by Eq. (2):

$$J_w = \frac{V}{A \times \Delta t} \tag{2}$$

where J_w is the volumetric permeate water flux (L m^{-2} h^{-1}), A is the effective area of the membrane for permeation (m^2), and V is the volume of permeation (L) over a time interval Δt (h).

3. Results and discussion

3.1. Chemical composition and surface morphologies of membrane

The preparation process of the PTFE-CMC/PEI-GA membrane and the possible chemical reaction mechanism on the membrane are shown in Fig. 2. GA is widely used as a cross-linking agent due to its commercial availability, low cost and high reactivity [39]. Carbonyl groups in GA molecule can undergo nucleophilic addition reaction, and the positively charged carbonyl carbon atom is easily attacked by nucleophilic reagents. There is an unshared electron pairs in the nitrogen atom on the amino group of PEI, which makes it nucleophilic and easily reacts with the electrophilic carbonyl groups of GA through a Schiff base reaction, leading to the formation of a compound in which C=O bonds are replaced by C=N bonds. Moreover, the oxygen atom on the hydroxyl groups of CMC with negatively charged attributed to the charge polarization, which makes it react with GA through acetal reaction likely. The three cross-linked products were possibly assembled to form a large three dimensional network structures due to the electrostatic interaction between the –COO$^-$ group in CMC and the –NH$_3^+$ group from PEI [40].

3.1.1. Surface chemical structure of membranes

The surface chemical compositions of the original and modified membranes were studied using XPS. As illustrated in Fig. 3a, the original and PTFE-CMC/PEI membranes only show peaks of C1s and F1s at 284.81 and 689.1 eV, respectively. Compared with the above-mentioned membranes, the PTFE-CMC/PEI-GA membrane appears new peaks of N1s, O1s and Na1s at 398.81, 531.72 and 1,070.57 eV, respectively. The N element is derived from the amino groups of PEI, O element is derived from CMC and GA, and the Na element is derived from CMC. The results clearly show that CMC and PEI are successfully incorporated into the modified membrane. In addition, Table 1 shows the elemental compositions of different PTFE flat membranes, and the results are consistent with the XPS spectra.

To further illustrate the cross-linking reaction. Gauss fitting method was applied to study the high-resolution XPS spectrum of C1s (Fig. 3b–f) [41]. As shown in Fig. 1b and c, the C1s core-level spectrum was curve-fitted with two main peak components at 292.20 eV for C–F and 284.82 eV for C–C, demonstrated that CMC and PEI cannot react without GA. As for the PEI-GA PTFE membranes, besides C–F and C–C, three peaks were found at 284.88 eV
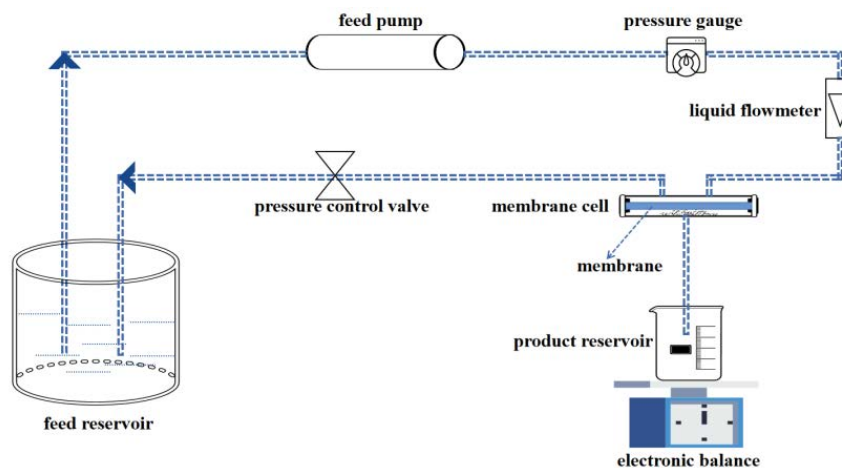

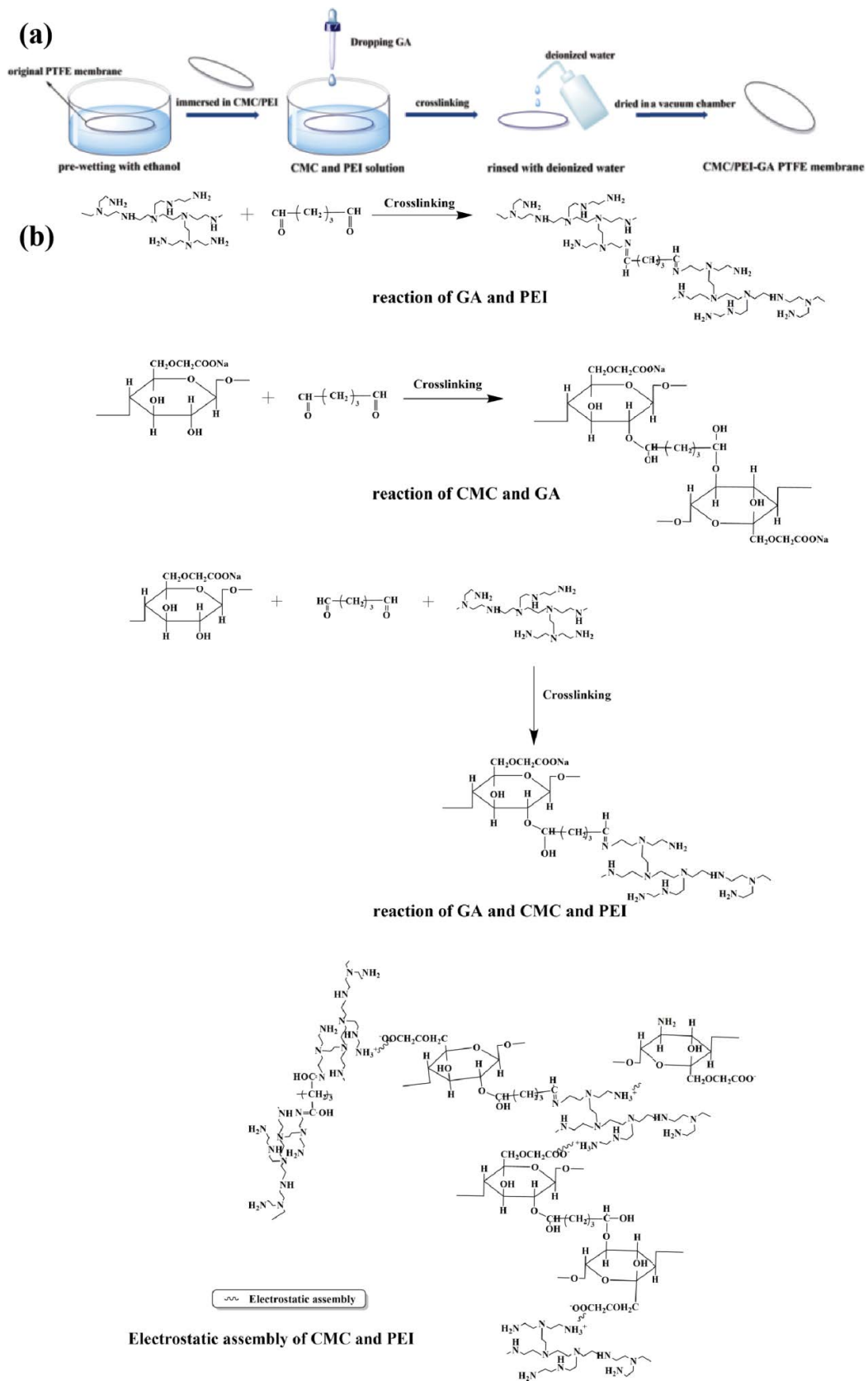Fig. 1. Schematic diagram of the cross-flow device.

Fig. 2. Schematic illustration for CMC/PEI modified PTFE membrane (a) and possible chemical reaction mechanism on PTFE membrane (b).

Table 1
Elemental composition of the original PTFE and modified PTFE membranes as determined by XPS

Membrane	Composition (at.%)				
	C	F	O	N	Na
Original PTFE	33.17	66.83	/	/	/
PTFE-CMC/PEI	33.79	66.21	/	/	/
PTFE-CMC/PEI-GA	41.55	44.4	6.38	7.16	0.51
PTFE-CMC-GA	36.06	62.95	0.6	/	0.39
PTFE-PEI-GA	37.01	59.61	1.71	1.67	/

(C–N), 285.68 eV (C=N) and 286.78 eV (C=O), respectively (Fig. 3f). The C=O species was introduced by GA, the C–N species was introduced by PEI, and the C=N species was formed by Schiff base reaction between amino group of PEI and carbonyl groups of GA. Besides five peaks mentioned above, a new peak was found at 285.48 eV in the PTFE-CMC/PEI-GA membrane for C–O, which was introduced by CMC (Fig. 3d and e).

The chemical composition of different membranes were characterized by ATR-FTIR analysis, as shown in Fig. 4. The original PTFE membrane and the PTFE-CMC/PEI membrane showed two characteristic peaks at 1,151 and 1,211 cm^{-1}, respectively, which are corresponding to the stretching vibration of –CF$_2$ groups. Addition of GA resulted in three stretching vibration peaks for –CH$_2$ (2,930 and 2,862 cm^{-1}) and C=O at 1,648 cm^{-1}, respectively. The –CH$_2$ species is derived from GA, the C=O species may be attained from CMC molecule or one carbonyl group of GA that didn't react with the amino group of CMC and PEI. Compared with the PTFE-CMC-GA membranes, the PTFE-PEI-GA and PTFE-CMC/PEI-GA membranes appeared a new absorption band at 1,542 cm^{-1}, which is assigned to C=N stretch vibration. As a result, CMC and PEI could not react without adding GA, which was also confirmed by the XPS results shown above. Moreover, the broad peaks at 3,500–3,200 cm^{-1} may belong to V_{O-H} and V_{N-H}, V_{O-H} was attained from CMC and V_{N-H} may come from unreacted PEI. The results prove that CMC and PEI were successfully introduced into the PTFE-CMC/PEI-GA membrane.

3.1.2. Surface morphological structure of membranes

The surface morphological alteration in the different membranes were characterized by FESEM (Fig. 5). The original PTFE membrane (Fig. 5a) was composed of nodes and fibrils. It can be clearly observed that the modified PTFE membrane (Fig. 5b) which at optimal conditions (reaction time is 6 h, CMC/PEI mass ratio is 4:1, the GA concentration is 5 g L^{-1}, concentration of CMC is 5 g L^{-1} came to form a coating layer on the nodes and fibers, but there was no blockage occurs. The PTFE-CMC-GA membrane (Fig. 5c) and the PTFE-PEI-GA membrane (Fig. 5d) were also coated with a hydrophilic layer, but the coating on the PTFE-PEI-GA membrane surface was more dense. Compared with other modified membranes, the PTFE-CMC/PEI membrane (Fig. 5e) had no obvious particles attached to the fibers. The pores on the surface of

PTFE modified membrane were come to smaller and even blocked as the concentration of CMC and PEI increased (Fig. 5f and g). Overmuch GA brings about larger particles formation, leading to micropore blockage (Fig. 5h), it can be explained by excessive cross-linking of the reaction system. As reaction time exceeds 6 h, a dense layer was formed on the surface of membranes (Fig. 5i). This phenomena may be accounting to that the three cross-linked products were possibly electrostatic assembled to form a larger three-dimensional network molecular structure.

The cross-section of the PTFE-CMC/PEI-GA membrane scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) scan images are shown in Fig. 6. The original PTFE membranes were formed by biaxial stretching and composed of fibers and nodes. It can be seen from the cross-section of the original membrane that there are many nodes inside (Fig. 6a). Compared to the original membrane, the modified membrane cross-section is clearly different, and the PTFE nodes are wrapped by a layer of material (Fig. 6b). By comparing Fig. 6c and d, it can be seen that the O, N and Na elements appeared in cross-section of PTFE-CMC/PEI-GA membrane, indicating that the whole membrane is well modified. The main reason is that the modification process is occurred in a homogeneous solution, and the three-dimensional network material formed by cross-linking and wrapped the PTFE fibers and the nodes, the inner morphology of the membrane pores is also changed.

3.2. Surface water permeability and wettability of membranes

The water permeability and wettability of the modified PTFE membranes were evaluated by pure water flux (J_w) tests and water contact angle (WCA), respectively.

The effect of CMC concentration on J_w and WCA is shown in Fig. 7a. PEI-GA PTFE membrane is hydrophilic (J_w is 3,420 ± 190 L m^{-2} h^{-1}, WCA is 84.9° ± 2.4°), owing to the amino groups (–NH$_2$) on PEI molecule. The J_w increases with the increasing of CMC concentration before the CMC concentration reaches to 5 g L^{-1}. In addition, WCA decreases with the increasing of CMC concentration. The J_w reaches to the maximum value when the concentration of CMC is 5 g L^{-1}, the best J_w and WCA is 4,485 ± 187.4 L m^{-2} h^{-1} and 45.6° ± 2°, respectively. However, the J_w began to remarkably decrease when continue increasing CMC concentration, and the corresponding WCA increases. This result may be attributed to that high concentration of CMC self-crosslinking brings about hydrophobic products and blockage of the pores. The mass ratio of CMC and PEI also plays an important role in membrane hydrophilization (Fig. 7b). For the PTFE-CMC-GA membrane without PEI, J_w is 0 L m^{-2} h^{-1}, WCA is 120° ± 3°. The value of J_w and WCA is optimal when the mass ratio of CMC and PEI is 4:1. As the mass ratio of CMC and PEI changed to 3:1, it can be seen that the hydrophilicity of the modified membrane showed a significant downward trend, the J_w and WCA is 2,584.4 ± 198.4 L m^{-2} h^{-1} and 63.4° ± 2.6°, respectively. When the mass ratio of CMC and PEI was 1:1, the J_w is decrease to 2,194 ± 200 L m^{-2} h^{-1} and WCA is increase to 75.6° ± 2.6°, respectively, which may be caused by partly pores blockage due to an excessive amount of PEI. Moreover, the effect
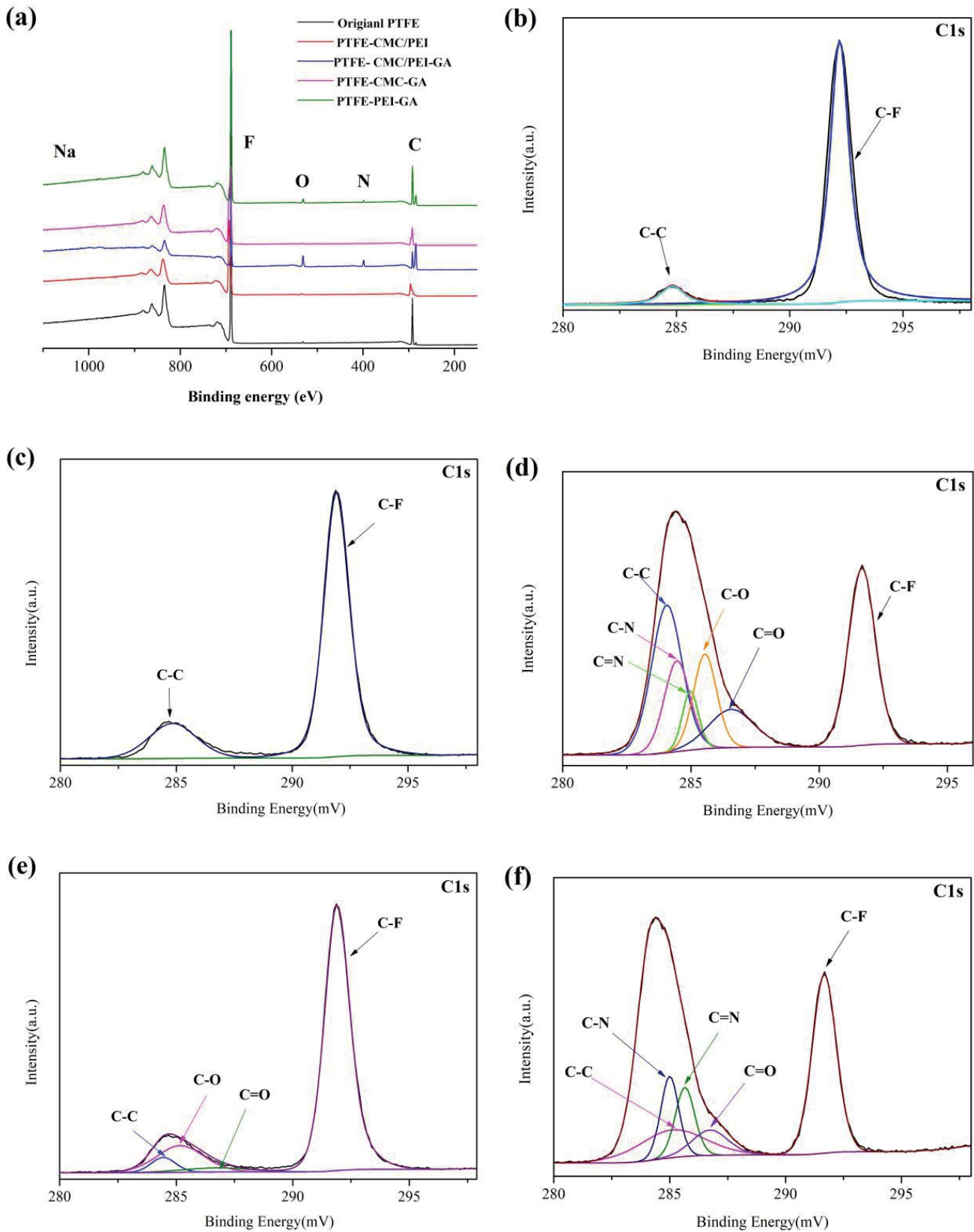
Fig. 3. XPS spectra of the original PTFE and modified PTFE membranes (a) and C 1s core level spectra resolving results of membranes original PTFE (b), PTFE PTFE-CMC/PEI (c), PTFE-CMC/PEI-GA (d), PTFE-CMC-GA (e), and PTFE-PEI-GA (f).
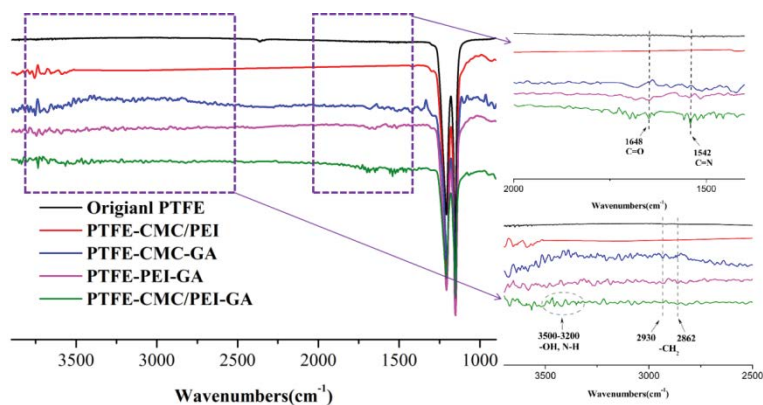
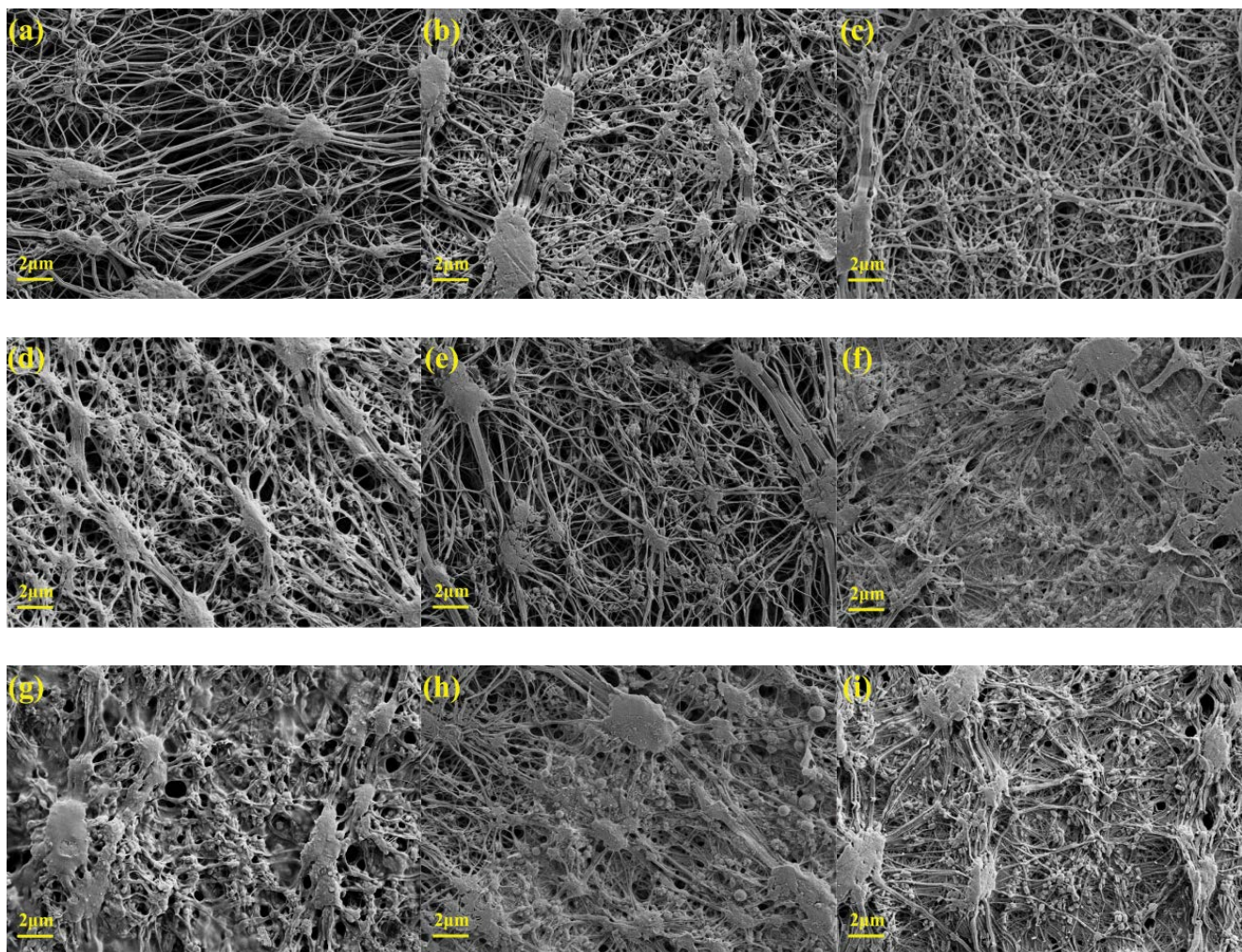Fig. 4. ATR-FTIR spectra of the membrane.

Fig. 5. SEM images of different PTFE membrane: (a) original PTFE, (b) PTFE-CMC/PEI-GA (CMC:PEI = 4:1), (c) PTFE-CMC-GA, (d) PTFE-PEI-GA, (e) PTFE-CMC/PEI, (f) PTFE-CMC/PEI-GA (concentration of CMC is 20 g L⁻¹), (g) PTFE-CMC/PEI-GA (OCMCS/PEI mass ratio is 1:1), (h) PTFE-CMC/PEI-GA (concentration of GA is 9 g L⁻¹), and (i) PTFE-CMC/PEI-GA (reaction time is 24 h).

of cross-linking reaction time on J_w and WCA were investigated (as shown in Fig. 7c). The hydrophilicity of the modified membrane increases firstly and then decreases with the increase of reaction time. The J_w increased from 2,457.4 ± 179.3 L m⁻² h⁻¹ to 4,485 ± 187.4 L m⁻² h⁻¹, and the corresponding WCA is decrease from 88.3° ± 2.3° to 45.6° ± 2°. However, the hydrophilicity of the modified membrane decreases with cross-linking time extending to 6 and 24 h.
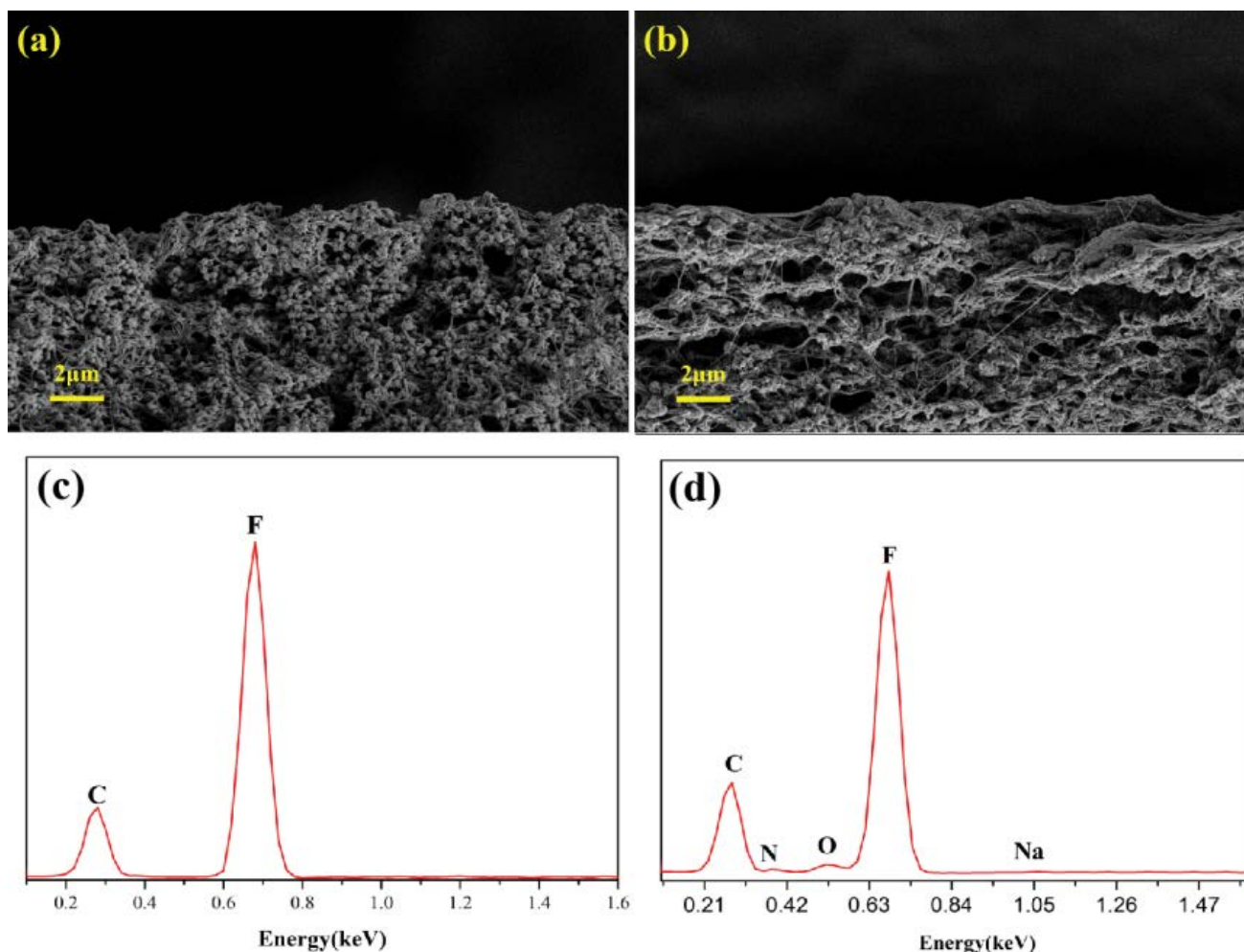
Fig. 6. Cross-section SEM (a) and EDS (c) of original PTFE, cross-section SEM (b) and EDS (d) of PTFE-CMC/PEI-GA membrane.

When the cross-linking time is 24 h, the J_w is decrease to 3,113.05 ± 178.9 L m^{-2} h^{-1}, WCA is increase to 79.9° ± 2°. It seems possible that this result is ascribed to electrostatic assemble of the three cross-linking products to form a larger three-dimensional network molecule structure blocking the pores.

The effect of GA concentration on the hydrophilicity of the modified PTFE membrane was investigated as shown in Fig. 7d. In the absence of GA, the PTFE-CMC/PEI membrane was a hydrophobic membrane with J_w of 0 L m^{-2} h^{-1} and WCA of 115.8° ± 2.8°, which is similar to the original ones. This result indicates that GA is indispensable for hydrophilic modification of the PTFE membrane. After adding GA, it can be found that J_w of the modified membrane increased firstly and then decreased with elevated the concentration of GA. This phenomenon may be attributed to high concentration of GA which consumes a large number of amino groups on PEI make the hydrophilic group decreased. According to this study, the optimal concentration of GA is 5 g L^{-1}, the corresponding J_w is 4,458 ± 187.4 L m^{-2} h^{-1} while WCA is 45.6° ± 2.0°.

Based on the above results, the optimal reaction conditions are as follows: the concentration of CMC, the mass ratio of CMC and PEI, GA concentration, cross-linking time were 5, 4:1, 5 and 6 h respectively, all the following experiments were conducted on this membrane.

3.3. Separation of oil/water emulsions with the modified membranes

To determine the superiority of the modification method in constructing superwetted surfaces, the wettability of these investigated membrane were compared. By comparison, the membrane after synergistic modification of CMC and PEI has a high degree of hydrophilicity and excellent underwater superoleophobicity, and its UWOCA (dichloromethane) is as high as 151.47°. This result can be attributed to the combined effect between the synergistic deposition of hydrophilic CMC/PEI-GA and the rough nanostructure morphology.

Inspired by its superior underwater anti-oil-adhesion property, the membrane was tested for its underwater self-cleaning performance as a proof-of-concept study. As indicated in Fig. 9, original PTFE membrane exhibited severe oil-fouling and oil-adhesion behaviors, indicating that it has scarcely any self-cleaning performance underwater.
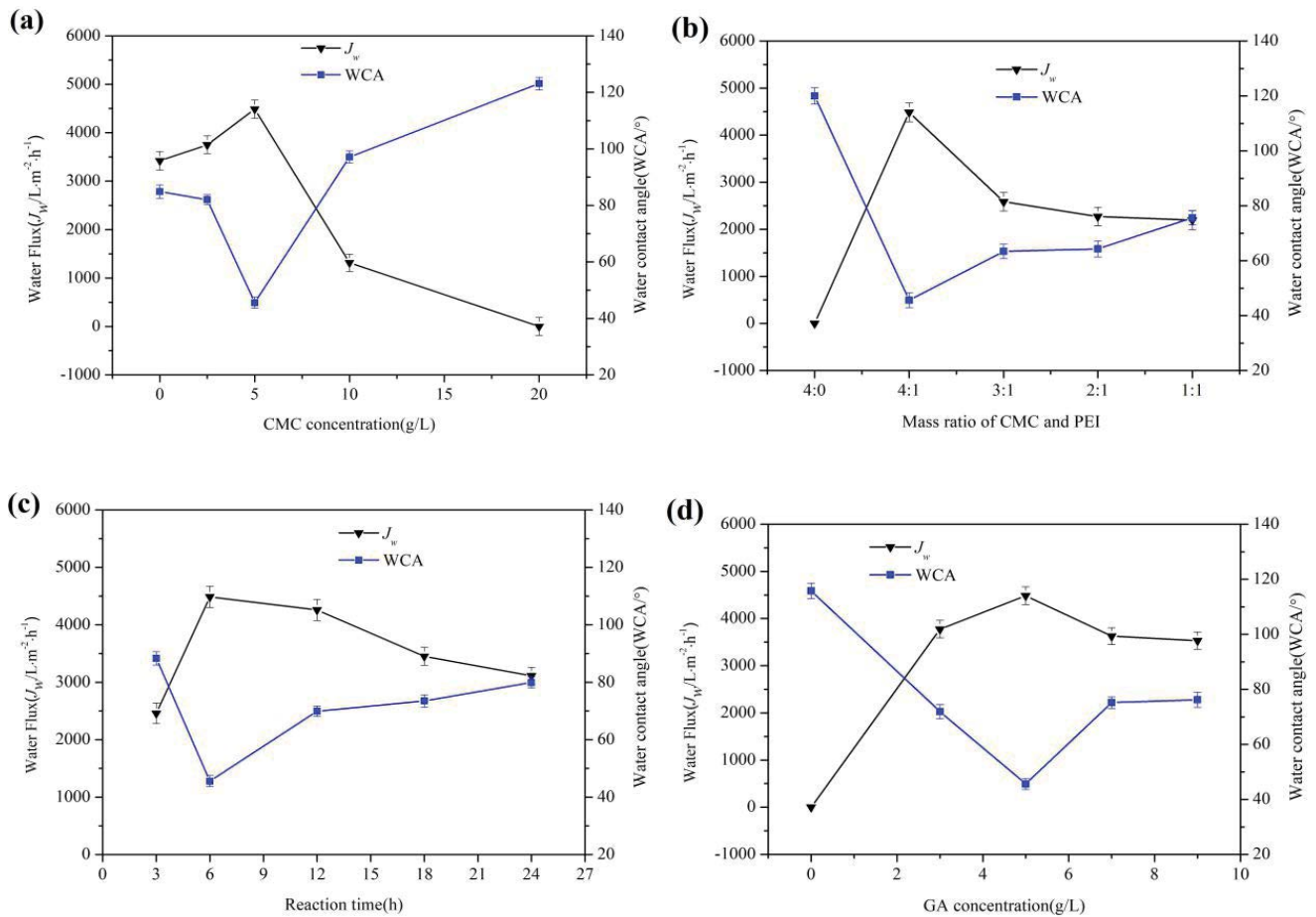
Fig. 7. Effect of reaction condition (a) concentration of CMC, (b) CMC:PEI (mass ratio), (c) reaction time, and (d) GA concentration on contact angle and water flux of modified PTFE flat membrane.

In contrast, as for PTFE-CMC/PEI-GA membrane, it can be seen from Fig. 9a that when the vegetable oil is jetted on the membrane surface, vegetable oil can immediately bounce off the membrane surface without leaving any oil droplet. Furthermore, when the vegetable oil adhered pre-wetted membrane in air was immersed into water, the spreading oil layer could spontaneously shrink into a spherical oil droplet and then completely detach from the surface in a short time (Fig. 9b). Therefore, these results strongly demonstrate the remarkable underwater self-cleaning performance of PTFE-CMC/PEI-GA membrane.

The separating results of oil/water emulsion are shown in Fig. 10. The size of oil droplets in milky emulsion mainly ranges from 28.21 to 6,439 nm (Fig. 10b), the color of oil/water emulsion is milky and the filtrate becomes clear after filtration (Fig. 10a), indicating that most of the oil in water was removed. The oil/water emulsion rejection ratio and permeation flux of the membrane are shown in Fig. 10c. The oil rejection of the PTFE-CMC/PEI-GA membrane towards oil/water emulsion is above 97.8%, while the permeation flux is as high as 1,047.23 L m^{-2} h^{-1} under 0.05 MPa. The pore-size distribution of the different PTFE membranes is shown in Fig. 10d, the pore size of the PTFE flat membranes decreased after modified by
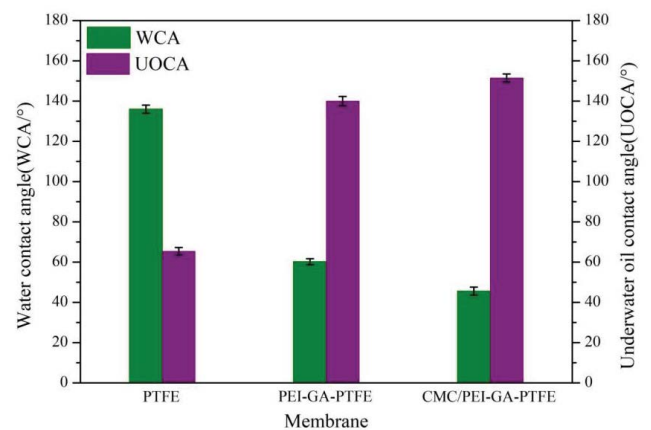

Fig. 8. Surface wetting properties of the membranes (the oil is dichloroethane).

CMC/PEI-GA. The mean pore size of the original PTFE and PTFE-CMC/PEI-GA membranes is 183.3 nm 163.1 nm.

Comparison of the membrane hydrophilicity and oil/water emulsion separation performance with other PTFE
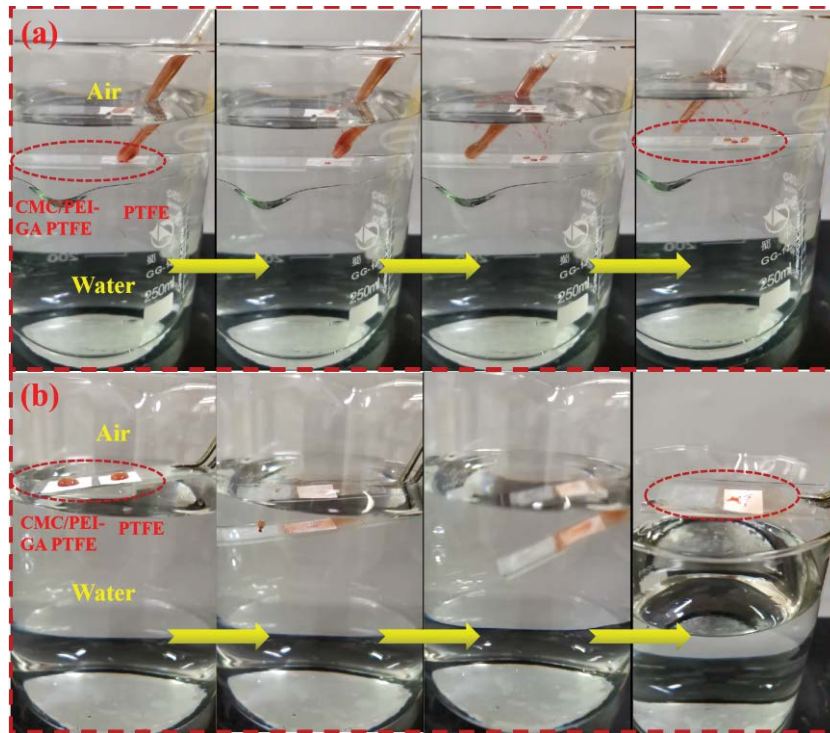
Fig. 9. Anti-oil adhesion (a) and self-cleaning properties (b) of the membrane (vegetable oil).
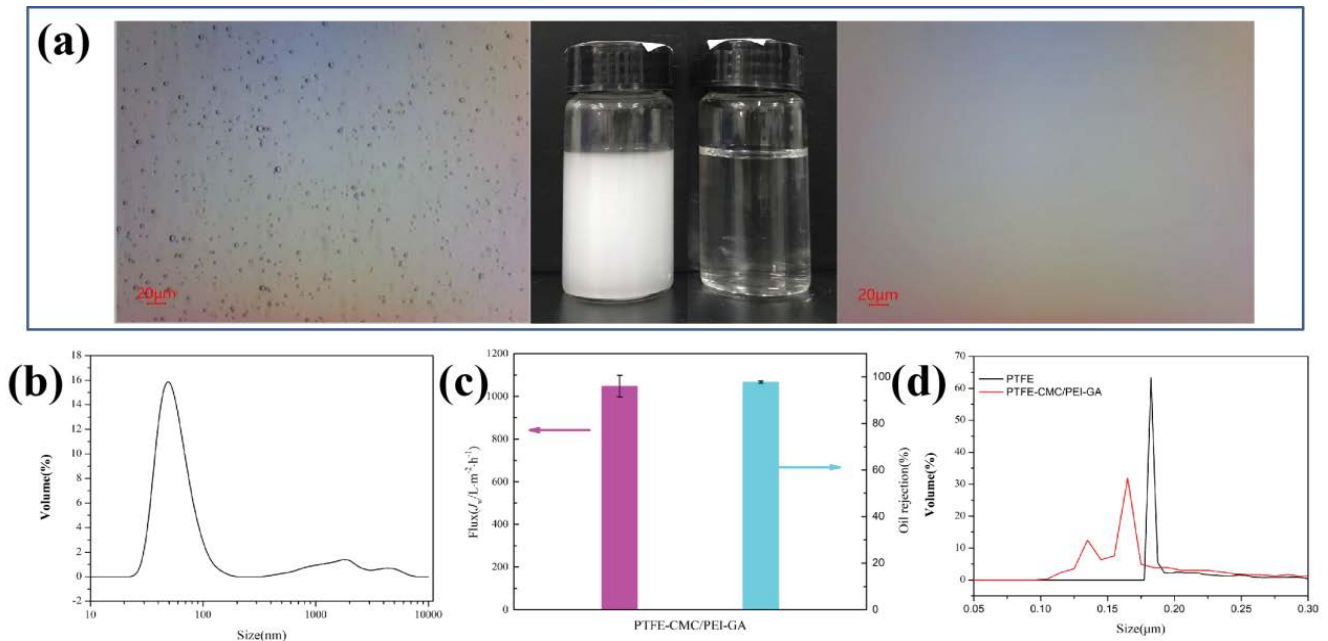

Fig. 10. (a) Optical micrographs of emulsions before and after separation, (b) DLS data of the oil/water emulsion, (c) flux and oil rejection of the PTFE-CMC/PEI-GA membrane, and (d) pore-size distribution map of different PTFE membranes.

hydrophilic membrane (Table 2), the PTFE-CMC/PEI-GA membrane have shown their superior hydrophility and oil/water emulsion separation performances. Such exceptional underwater superoleophobicity and oil resistance of

membrane may be derived from the following key factors: (i) CMC has high hydration capacity, and there is exhibits excellent water-absorbing and water-retaining capacities through strong hydrogen-bonding interactions between

Table 2
Comparison of the membrane hydrophilicity and oil/water emulsion separation performance with other PTFE hydrophilic membrane

Membrane	Water contact angle (°)	Separation flux (L m^{-2} h^{-1})	Pressure (bar)	Oil rejection (%)	References
PTFE-CMC/PEI-GA	45.6	1,047.23	0.5	98.6	This work
PTFE-PVA/CS-SiO$_2$	46.7	215.76	0.1	97.67	[4]
PTFE-OCMCS/PEI-GA	69	/	/	/	[27]

water molecules and CMC segments, resulting in a highly stable hydration sheath on the surface; according to the classical Cassie model (oil/water/solid three-phase interface) [42], the dense hydration layer as a strong barrier can effectively prevent oil droplets from directly contacting and adhering to the surface, thereby significantly reducing the area of contact with the oil with the surface, thus achieving excellent oil repellency. (ii) The rough network forms many nanocavities and provides more space to trap water, which clearly promotes the formation of the Cassie state.

3.4. Stability evaluation of modified membranes

Membrane fouling is the major obstacle in membrane separation technology, which not only decreases the filtration efficiency, but also shortens the lifetime of the membrane [43]. In this paper, three cycles of the oil/water emulsion filtration experiment was carried out to evaluate the anti-fouling performance of the PTFE-CMC/PEI-GA membrane. The permeation flux value of each filtration is shown in Fig. 10. It can be seen that the permeation flux of modified membranes declined sharply with the increase of time due to the formation of oil cake on membrane surfaces, but the flux can be recovered to a certain extent after only simple rinsing with water. These results indicate that both the PTFE-CMC/PEI-GA membranes possess an excellent anti-fouling performance and long-term usage.

Mechanical stability of the hydrophilic coating on the surface of the modified PTFE membranes is also very important in practice. In order to identify the mechanical stability of the coating on the membrane, the durability of surface coatings has been studied by pure water filtration process for 24 h under the pressure of 0.1 MPa. The results are shown in Fig. 12. The J_w of the PTFE-CMC/PEI-GA membranes decreases first and then tends to be stable with the increase of rinse time, while WCA increases first and tends to be stable. The reason is that small particles in water will be deposited in the membrane pores in the process of continuous filtration, resulting in a decrease in pure water flux. These results indicate that the hydrophilic coating on the membrane shows superior stability.

4. Conclusion

In summary, a novel and facile method was developed to modify the PTFE membrane by cross-linking CMC and PEI with GA. ATR-FTIR and XPS analysis confirmed that CMC and PEI were introduced into PTFE membrane successfully. The hydrophilic group (such as –NH$_2$, –OH) were found on surface of PTFE-CMC/PEI-GA membrane
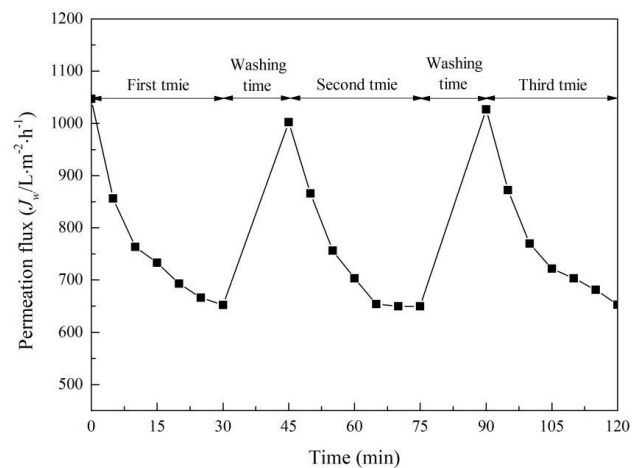

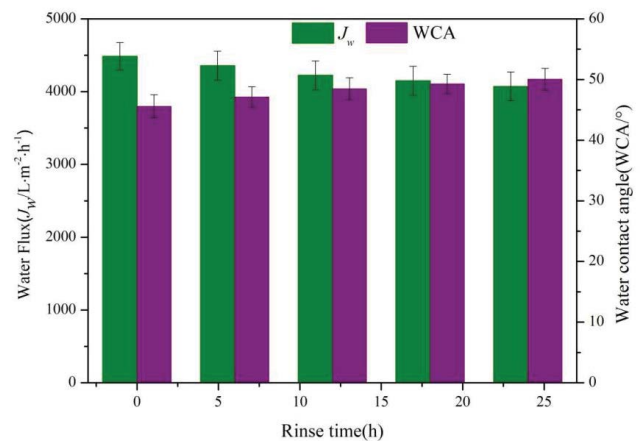Fig. 11. Flux of oil/water emulsions and flux recovery over three cycles.

Fig. 12. Stability of the PTFE-CMC/PEI-GA membrane.

via ATR-FTIR and XPS analysis; It was observed by FESEM that the surface of PTFE-CMC/PEI-GA membrane which modified under the best condition coated with hydrophilic layer, but there was no pore blocked on the surface of the membrane; Under optimal reaction conditions, the PTFE-CMC/PEI-GA membrane J_w is 4,458 L m^{-2} h^{-1} while WCA is 45.6°; Meanwhile, the oil rejection is above 97.8%, while the permeation flux is as high as 1,047.23 L m^{-2} h^{-1} under 0.05 MPa. The PTFE-CMC/PEI-GA

membrane was endowed with excellent hydrophilicity, anti-fouling property, self-cleaning property and long-term operational stability. Besides, due to the simple and eco-friendly fabrication procedure, the modified membrane shows a promising future in practical application.

Conflict of interest

The authors declare no competing financial interest.

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