Plasma-assisted facile fabrication of omniphobic graphene oxide membrane with anti-wetting property for membrane distillation

Huimin Chen\textsuperscript{a}, Yangyang Mao\textsuperscript{a}, Binyu Mo\textsuperscript{a}, Yang Pan\textsuperscript{a,b}, Rong Xu\textsuperscript{b,***}, Wenqi Ji\textsuperscript{a}, Guining Chen\textsuperscript{a,***}, Gongping Liu\textsuperscript{a}, Wanqin Jin\textsuperscript{a}

\textsuperscript{a} State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 30 Pu Zhu Road (S), Nanjing, 211816, China
\textsuperscript{b} Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Gehu Road, 213164, Changzhou, China

\textbf{ARTICLE INFO}

Audits: graphene oxide membrane, omniphobic membrane, plasma treatment, surface modification, membrane distillation

\textbf{ABSTRACT}

Novel design of omniphobic membrane could relieve the wetting phenomenon caused by low surface energy contaminants in the feed of membrane distillation process. In this work, we reported on a new kind of omniphobic graphene oxide (GO) membrane fabricated by plasma treatment and subsequent fluoroalkyl grafting of stacked GO laminates. The plasma treatment not only created in-plane nanopores in GO nanosheets to provide more water channels, but also added active sites for fluoroalkyl grafting to build a robust omniphobic membrane surface. The resulting omniphobic membrane exhibited outstanding water flux of ~35 kg m\textsuperscript{-2} h\textsuperscript{-1} and salt rejection of 99.9% for 35 g L\textsuperscript{-1} NaCl solution with 0.2-0.4 mM sodium dodecyl sulfate (SDS) at 60 °C during over 450 h of direct contact membrane distillation (DCMD) process. This work provides a facile strategy to develop high-flux and wetting-resistance materials for membrane distillation.

1. Introduction

Membrane distillation (MD) is an emerging separation technology that combines membrane separation and evaporation [1]. In MD process, the vapor transport through the porous and hydrophobic membrane is driven by the temperature difference of both sides of the membrane [2]. Compared with traditional membrane desalination process, MD has the advantage of a high salt rejection rate, and water flux is almost not affected by the salt content of the raw material [3,4]. Although membrane distillation has many benefits, its application in treating industrial wastewater still faces challenges, such as wetting and fouling phenomenon, temperature and concentration polarization, lower flux and higher energy consumption compared with other membrane separation processes [5-7]. Among these, the greatest challenge is membrane wetting during MD process [8]. As feed solution contains low surface energy contaminants, such as organic pollutants and surfactants, conventional hydrophobic membranes generally suffer from membrane wetting [9]. When static pressure across the membrane exceeds the liquid entry pressure (LEP), membrane will be wetted. What’s more, capillary condensation, chemical and mechanical degradation of membrane in the long-term MD process will also lead to membrane wetting [10].

Omniphobic membranes have been demonstrated to effectively relieve membrane wetting caused by low surface energy contaminants [3,11]. The typical strategy for fabricating an omniphobic surface is to combine re-entrant morphology fabrication and surface free energy reduction [12,13]. Usually, incorporating nanoparticles into the membrane layers can enhance surface roughness, and be convenient for subsequent fluoroalkyl grafting to obtain low surface free energy [14,15]. Elimelech and co-workers proposed an omniphobic microporous membrane fabricated by coating silica nanoparticles on hydrophilic glass fiber membrane and then fluorination modification [11]. Compared with commercial PTFE membrane, the omniphobic membrane exhibited robust performance in direct contact membrane distillation (DCMD) using 1.0 M NaCl with 0.1-0.4 mM SDS as feed solution. Lu and co-workers also prepared an omniphobic membrane via depositing silica nanoparticles on the surface of the PVDF hollow-fiber membrane and then coating Teflon AF [16]. During 7 h vacuum
membrane distillation (VMD) tests, this omniphobic PVDF membrane showed stable performance as feed solution containing low surface tension substances. Electrospun membranes play an increasingly significant role in desalination due to their immense porous surface, high porosity, controllable pore sizes and membrane thickness [3]. In addition, different functional particles can be incorporated while producing electrospun membranes to achieve higher mechanical strength and omniphobicity. It was demonstrated that an omniphobic electrospun membrane of PVDF-HFP and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS) displayed stable water flux and quality in saline membrane of PVDF-HFP and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS) displayed stable water flux and quality in saline membrane of PVDF-HFP and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS) displayed stable water flux and quality in saline membrane of PVDF-HFP and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS), which would create a robust omniphobic surface. Hence, this plasma-assisted fabrication strategy can simultaneously enhance the water flux, salt rejection and wetting resistance of graphene-dominated membrane.

2. Materials and methods

2.1. Materials and chemicals

Graphene oxide (GO) aqueous dispersion was purchased from Hangzhou Gaoxi Technology Co., Ltd., China. Polyvinylidene difluoride (PVDF) powder with molecular weight of $5.0 \times 10^5$ was purchased from Kureha Co., Ltd., Japan. 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (fluorinated alkyl silane, FAS), humid acid (HA) and isopropyl alcohol were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. Acetone was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. Deionized water was used in all the experiments. All materials were used without further purification.

2.2. Fabrication of omniphobic rGO membranes

PVDF solution was prepared by dissolving through stirring 12 h of 10 wt% PVDF in a mixed solvent composed of DMF and acetone (4:1 by wt.%). The resulting PVDF solution was loaded in the syringe of an electrospinning equipment to fabricate the electrospun PVDF membrane. 0.25 mg, 0.5 mg, 1 mg GO nanosheets were evenly dispersed into the solution composed of 50 g deionized water and 120 g ethanol by ultrasound 2 h and then deposited on the electrospin polyvinylidene difluoride (PVDF) substrate via vacuum filtration to obtain pure GO membranes. The pure GO membrane after drying at room temperature was exposed to air plasma to create in-plane nanopores at a power of 26
odecyl-triethoxysilane (fluorinated alkyl silane, FAS) for 24 h, and immersed in hexane solution containing 2% v/v 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (fluorinated alkyl silane, FAS) for 24 h, and thermally treated at 140 °C for 1 h. GO reduced by heat treatment is called reduced GO (rGO). Hence, this membrane was signed as rGO-P-FAS (Fig. 1). The omniphobicity of rGO-P-FAS membranes was mainly from the fluoroalkyl grafting and thermal reduction. Fluorine-containing reagents can impart very low surface free energy to the membrane, resulting in an omniphobic surface. In addition, the heat treatment at 140 °C was performed to covalently bind the fluoroalkyl chains and to remove the excess oxygen-containing groups on GO. As a control, the GO membrane directly grafted with FAS and thermally treated without plasma treatment was marked as rGO-FAS.

2.3. Membrane characterizations

The lateral size and thickness of the GO nanosheets after ultrasound, and roughness of membranes were obtained from the atomic force microscope (AFM, Bruker Dimension Icon, USA). The surface and cross-section morphology and the thickness of rGO-P-FAS membranes were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi-4800, Japan) with Energy Dispersive X-Ray Spectroscopy (EDX) equipment. The FE-SEM was operated at 5 kV and 10 μA and EDX was operated at 20 kV and 10 μA. The in-plane nanopores of GO nanosheets created by plasma treatment were characterized by aberration corrected transmission electron microscopy (ACTEM, Themis Z, USA). The pore size distribution of PVDF substrates was measured by the bubble pressure method via the SYH-60 membrane performance analyzer (Shuyihui Scientific Instrument Co., Ltd, Nanjing, China). Porosity of composite membrane and support is tested by Archimedes method [25]. Surface wettability and surface free energy of the membranes were assessed by contact angle measurement (CA, Theta Flex, Biolin Scientific) of different liquids. Fourier transform infrared (FTIR, PerkinElmer, USA) spectroscopy with a range of 4000–450 cm⁻¹ was utilized to analyze the functional groups of the membrane. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA) was utilized to analyze the chemical properties of the membrane. X-ray diffraction (XRD, Rigaku Miniflex 600, Japan) was conducted at the range of 5° ≤ 2θ ≤ 40°. The LEP of membranes was tested by homemade components for nanofiltration connected with a nitrogen cylinder.

2.4. DCMD desalination test

The water desalination performance and anti-wetting property of the membranes were evaluated by direct contact membrane distillation (DCMD) process with a membrane cell in a countercurrent crossflow mode, as shown in Fig. 2. The effective membrane area was 4.9 cm². The temperature of the feed (35 g • L⁻¹ NaCl solution) was maintained at 50–80 °C by using an oil bath, and permeate stream (deionized water) was maintained at 20 °C by using low temperature thermostat. In DCMD wetting tests, 35 g • L⁻¹ NaCl solution with 0.2 mM SDS and deionized water was used as the feed and permeate, respectively. Then, 0.05 mM SDS was added into feed solution every 2 h until the concentration of SDS reached 0.4 mM to explore the influence of SDS concentration on the performance of membranes. Organic fouling, such as HA, protein and polysaccharides, tends to adsorb/deposit on the membrane surface [10]. In MD fouling experiments, 35 g • L⁻¹ NaCl solution with 30 mg • L⁻¹ humic acid was used as the feed. The permeate flux and salt rejection of membranes were calculated by the rates of change in the distillate mass and salinity, respectively. The weight change in the permeate was monitored by a digital balance with an accuracy of ±0.01 g. The permeate flux (J, kg • m⁻² • h⁻¹) is calculated by the following equation [26]:

\[ J = \frac{\Delta W}{A \cdot \Delta t} \]  

(1)

where \( \Delta W \), \( A \), and \( \Delta t \) represent the mass increase of distillate, the effective area of membrane, and the interval time, respectively.

The conductivity of the permeate solution was monitored by a conductivity meter with built-in software. The salt rejection (R, %) is calculated by the following equation [26]:

\[ R = \frac{C_f - C_p}{C_f} \times 100\% \]  

(2)

where \( C_f \) and \( C_p \) refer to the salt concentrations of the feed and distillate,

Fig. 2. Experimental set-up for direct contact membrane distillation.
3. Results and discussion

3.1. Membrane morphologies

As shown in Fig. 3a, the lateral size of the GO nanosheets for membrane fabrication was ~700 nm and the thickness was ~0.7 nm, which were analyzed by AFM. Such a high aspect ratio endows GO nanosheets being easily deposited on a porous substrate and assembled into GO laminates. In this work, the porous substrate with an average pore size of ~650 nm was prepared by electrospinning PVDF nanofibers (Fig. 3b and c). rGO and PVDF both have hydrophobic surfaces, which can form a relatively tight bond through a hydrophobic-hydrophobic interaction. To visualize the stability of rGO-P-FAS membranes, rGO-P-FAS membrane was treated by ultrasound in brine for 2 h and another one was soaked in brine for 1 week, respectively. From Fig. S1, no peeling sheets or apparent surface defects or damage were observed, indicating good adhesion between GO layers and the support.

As confirmed by SEM characterization, we could clearly observe that GO nanosheets were uniformly deposited on the PVDF nanofiber substrate (Fig. 4a). The nanofiber structure of the membrane surface was obvious, which is favorable for increasing the surface roughness of the GO membrane. By controlling the deposition amount of GO nanosheets, the thickness of GO membrane layer was optimized at ~200 nm (Fig. 4b), as balancing the elimination of defects and reduction of transport resistance.

After treatment of plasma and/or FAS coating, the change of membrane morphology under SEM was not observed. There were no visible pores on the surface of rGO-P-FAS or rGO-FAS membrane, which is identical to that of the pristine GO membrane (Fig. 4c and d). Nevertheless, the plasma treatment can create in-plane nanopores of GO nanosheets, which were characterized by ACTEM. Fig. 5a and b shows the thermally reduced GO nanosheets before and after 5 s plasma treatment, respectively. The gray area was the graphene area, the bright white area was the functional group area (Fig. 5c), and the red circle highlighted irregular light gray area was attributed to nanopores [27]. The TEM results imply that more nanopores, with average size of less than 5 nm, were formed after plasma treatment, which could provide more transport channels for water across the GO membrane layer. However, it is difficult to measure the depth of these nanopores by TEM. To study the penetration depth of the nanopores, we added SEM images of rGO-P-FAS membranes with different GO deposition amounts. As shown in Fig. S2, thinner GO laminates were more fragile, leading to more large surface defects. It implied that when the thickness of GO membrane was reduced to ~100 nm, pores produced by plasma would penetrate the whole membrane. As the thickness of GO membrane increased to ~200 nm, pores could not penetrate the whole membrane. Hence, the penetration depth of nanopores could be estimated as between 100 and 200 nm.

3.2. Chemical and surface properties

FTIR characterization was utilized to investigate the chemical properties of pure GO, GO-P, rGO-P-FAS membranes and FAS reagent, as shown in Fig. 6a. In the spectra of GO and GO-P membrane, there are typical peaks of GO including hydroxyl group (3389 cm\(^{-1}\), –OH), carboxyl group (1761 cm\(^{-1}\), C=O; 1543 cm\(^{-1}\), C=O-H), aromatic ring (1625 cm\(^{-1}\), C=C) and epoxy group (1073 cm\(^{-1}\), C-O-C) [23]. Compared with GO, the peak intensity of –OH in GO-P membrane was increased, suggesting that plasma treatment added hydroxyl groups on the membrane surface. More hydroxyl groups meant that more active sites would be provided for subsequent fluorosilane grafting. The spectrum of rGO-P-FAS membrane appeared the peaks of Si–O–Si asymmetric vibrations (1087 cm\(^{-1}\)) and C–F stretching vibrations (1240 cm\(^{-1}\), –CF\(_2\); 1190 cm\(^{-1}\), –CF\(_3\)), corresponding to the characteristic peaks of FAS [28]. It suggested that FAS was introduced into the GO membrane.

Then XPS was further used to analyze the chemical bonding of the membranes. As shown in Fig. 6b, four typical peaks of GO were detected as C–C (284.8 eV), C–O (287.26 eV), C=O (288.76 eV) and O–C–O (289.46 eV) for pure GO membrane [23]. Deconvolution of the C1s spectrum of the rGO-P-FAS membrane showed two added peaks at 291.7 and 293.8 eV, which assigned to CF\(_2\)-CF\(_2\) and CF\(_2\)-CF\(_3\) groups, respectively [26]. The analysis of XPS also evidenced that fluoroalkyl chains were successfully grafted on the membrane surface. Moreover, the Si element (the yellow dot in Fig. 7) distribution on the surface of rGO-FAS and rGO-P-FAS was scanned by EDX. The yellow dots in the EDX image of rGO-P-FAS membrane surface were obviously more than rGO-FAS surface, which revealed that plasma treatment increased the

![Fig. 3](image-url) (a) AFM diagram of GO nanosheets; (b) SEM image and (c) pore size distribution of electrospun PVDF substrate.
Fig. 4. SEM images of (a) surface and (b) cross-section of rGO-P-FAS membrane, surface of (c) rGO and (d) rGO-FAS membrane.

Fig. 5. TEM images of (a) pristine rGO and (b) rGO-P-FAS nanosheets after thermal reduction.

Fig. 6. (a) FTIR spectra of pristine GO, GO-P, rGO-P-FAS membrane and FAS; XPS spectra of (b) rGO membrane and (c) rGO-P-FAS membrane.
grafting density of fluoroalkyl chains on the membrane surface.

The effect of plasma treatment time on the hydrophilicity of GO membrane surface was explored. As demonstrated in Fig. 8a, the water contact angle of GO membrane surface was gradually reduced from 42.5° to 16.3° as prolonging the plasma treatment time to 15 s. At the same time, plasma treatment also increases porosity of GO membranes (Table S1). The water contact angle on the 5 s plasma treated GO membrane surface kept decreasing from 35.4° to 23.8° within 250 s measurement period (Fig. 8b). Eventually, the GO membrane surface can be wet instantly by the water after 20 s plasma treatment. The highly enhanced surface hydrophilicity can be attributed to the more hydroxyl groups introduced on the GO nanosheets, which are favorable for increasing the grafting density of fluoroalkyl grafting based on the condensation reaction between C–OH of GO and Si–OH of FAS.

Although the surface of the membrane became more hydrophilic with the increasing time of plasma treatment, the SEM images showed that excessive plasma treatment also introduced large-sized defects in the membrane which would weaken the stability of membrane (Fig. S3). Moreover, roughness and layer spacing of GO membranes were hardly affected by plasma treatment, which were characterized by AFM (Fig. S4) and XRD (Fig. S5), respectively.

Furthermore, surface free energy and wettability of the membrane were evaluated by liquid-solid contact angle measurement. In this work, we measured contact angle on membrane surface using different typical liquids, including water, ethanol, diiodomethane and 35 g L⁻¹ NaCl containing 0.2 mM sodium dodecyl sulfate (SDS) (feed solution of DCMD). As shown in Fig. 9a, rGO-P-FAS membrane exhibited higher contact angles for all the liquids (i.e. water, 113.3 ± 1.2°; ethanol, 71.6 ± 0.6°; diiodomethane, 99.9 ± 1.5°; NaCl solutions with 0.2 mM SDS, 106.3 ± 0.4°) than rGO and rGO-FAS membranes. The results confirmed that an omniphobic rGO membrane was successfully prepared. Combining the moderate contact angle and the small pore size, the rGO-P-FAS membrane shows a high LEP value which means that the membrane is difficult to be wetted. The contact angles of water (polar liquid) and diiodomethane (non-polar liquid) were used to determine the surface free energy of the membranes, according to Owens-Wendt’s two-
liquid geometric mean method [29]. As shown in Fig. 9b, the order of surface free energy from low to high is rGO-P-FAS < rGO-FAS < rGO membrane (noting that all the membranes were thermally reduced at 140 °C for 1 h). Because FAS reduced the free energy of the surface of the membranes, rGO membranes with FAS coating had higher omniphobicity even if surface morphology of rGO, rGO-FAS and rGO-P-FAS membranes were almost the same. The lowest surface free energy (9.54 mJ m⁻²) in the rGO-P-FAS membrane suggests that the plasma treatment prior to FAS coating offers a more effective grafting of fluoroalkyl chains on the membrane surface than the direct FAS coating. In addition, the resulting omniphobic rGO-P-FAS membrane showed outstanding wetting resistance to the feed solution (35 g L⁻¹ NaCl containing 0.2 mM SDS).

3.3. Effects of GO deposition amount on DCMD performance

DCMD tests using 35 g L⁻¹ NaCl solution with 0.2 mM SDS at 60 °C as feed solution were performed to evaluate membrane desalination performance. The rGO-P-FAS membranes with deposition of 0.25 mg, 0.5 mg, and 1 mg were prepared to explore the effects of the deposition amount of GO nanosheets on DCMD performance. For comparison, we chose the water flux and salt rejection of these membranes after undergoing 1 h DCMD process. As displayed in Fig. 10, with the increase in GO deposition amount, the water flux showed a downward trend. Obviously, thickness addition caused the increase in transport resistance. When the GO nanosheets deposition was 0.25 mg, the flux was the largest, but the salt rejection decreased to 98% after DCMD testing for 1 h. Thinner GO laminates were more vulnerable, leading to more large surface defects and resulting in a decrease in salt rejection (Fig. S2). The high salt rejection was maintained when the GO deposition amount was 1 mg, but the flux was only 16 kg m⁻² h⁻¹. Therefore, 0.5 mg was considered as the optimal GO nanosheets deposition for the rGO membrane, which showed a balanced flux with salt rejection.

3.4. Effects of plasma treatment time on DCMD performance

Conditions of plasma treatment include current, voltage and treatment time. All these conditions had been optimized and the treatment time was found to be the most important factor affecting etching. Hence, we focused on the effects of different plasma treatment times on DCMD performance were tested under the same conditions as in section 3.3. Similarly, the water flux and salt rejection of these membranes after testing 1 h were chosen for comparison. As displayed in Fig. 11, with the increase in plasma treatment time, the membrane flux showed an upward trend, which proved that plasma treatment could indeed add more transport channels to improve water flux. Plasma treatment could introduce more oxygen-containing groups to facilitate the subsequent fluoroalkyl grafting, which could access to robust omniphobicity. On the other hand, plasma treatment produced some nanopores less than 5 nm in diameter (as indicated by TEM images in Fig. 5b). The flux increased without loss of salt rejection when the nanopores with suitable size, and these nanopores were considered as efficient nanochannels. Once the plasma treatment time was extended to 10 s long or more, pores larger than 1 μm were produced, making the membrane more vulnerable during the long-term stability. At this point, these micron-sized pores act as defects which are not useful for MD. Considering the membrane separation performance and stability, a plasma treatment time of 5 s was considered to be the optimal condition.

3.5. Stability of rGO-P-FAS membrane

Fig. 12a compared the DCMD desalination performances of rGO membranes with different preparation conditions. The red plots in Fig. 12a showed that the pristine rGO membrane with 140 °C thermal reduction was wetted after running only 70 min DCMD, as reflected by the rapid drops of flux and salt rejection. The green squares represented the rGO-FAS membrane undergoing ~12 h of testing, during which the water flux dropped to ~10 kg m⁻² h⁻¹ while the salt rejection slowly decreased. It suggests a typical wetting phenomenon that might be caused by the low/weak grafting density of fluoroalkyl chains on the GO nanosheets. Moreover, the water flux of rGO-P-FAS membranes with 5s and 10s plasma treatment time (signed as rGO-P-5s-FAS and rGO-P-10s-FAS, respectively) were significantly higher than that of rGO and rGO-FAS membranes, suggesting that the nanopores created by plasma treatment provided additional channels for water vapor transport while effectively rejecting the water liquid. The less stable flux of rGO-P-10s-FAS membrane was caused by membrane wetting during DCMD process.

Subsequently, continuous DCMD process of rGO-P-FAS membranes with different plasma treatment time was tested. Although the initial flux of rGO-P-10s-FAS membrane was higher than that of rGO-P-5s-FAS membrane, the flux and salt rejection began to decline after testing 30 h (Fig. 12b). However, the DCMD testing time of the omniphobic rGO-P-5s-FAS membrane was greatly improved, showing a high and stable flux and salt rejection during the DCMD process even over 450 h (Fig. 12c). During the first 370 h of the test with feed solution containing 35 g L⁻¹ NaCl solution and 0.2 mM SDS, the water flux (~35 kg m⁻² h⁻¹)
and salt rejection (99.99%) of the membrane have remained. In the subsequent test, the SDS concentration on the feed solution was increased to 0.4 mM. Then the flux of the membrane slowly decreased to about 31 kg m$^{-2}$ h$^{-1}$, and the salt rejection slightly decreased to 99.99%. Nevertheless, the MD process was kept stable for another 80 h continuous test. The obviously enhanced stable DCMD operating time in the rGO-P-FAS membrane can be attributed to that plasma treatment introduced more active sites to generate high density and robust fluoroalkyl grafting on the GO membrane surface.

For comparison, we summarized the state-of-the-art omniphobic membranes for DCMD process as feed solution containing low surface energy contaminants (as shown in Fig. 12d and Table S2) [4,26,30–40]. These omniphobic membranes were mainly based on hydrophobic polymers such as PTFE and PVDF. Most of them only have been tested with stable performances for about 10 h (Table S2 listed the detailed DCMD desalination test conditions and results of these membranes). One of primary metrics for measuring membrane wettability is liquid entry pressure (LEP), affected by the surface energy of the material, surface tension of feed solution, and membrane pore size and geometry. LEP is defined as [41]:

$$\text{LEP} = - \frac{B \gamma_l \cos \theta}{\gamma_{\text{max}}}$$  \hspace{1cm} (3)

where $\gamma_l$ is the surface tension of a liquid, $\theta$ is the apparent contact angle (CA) between feed solution and membrane surface, $\gamma_{\text{max}}$ is the maximum pore size of the membrane, and $B$ is the pore geometry coefficient ($B = 1.0$ for a circular pore). The LEP$_{\text{sw}}$ value of rGO-P-FAS membrane is 3.8 ± 0.2 bar, which is higher than reported values of other omniphobic membranes [31,42–44]. Moreover, existence of low surface surfactants, such as SDS, would reduce the surface tension of the feed solution. LEP is linearly proportional to surface tension, so surfactants in the feed solution make wetting easier. Therefore, it is difficult for existing membranes to undergo long-time DCMD process. Compared with them, the rGO-P-FAS membrane showed excellent stability and water flux in DCMD process. There are no defects on the surface of rGO-P-FAS membrane. Water vapor transported across this membrane mainly by the interlayer channels of GO nanosheets and the in-plane nanopores produced by plasma treatment. The size of these pores is much smaller than that of PVDF or PTFE membranes. In the case of the same feed solution, smaller pores of the membrane will create higher LEP, leading the membrane more difficult to be wetted. Thanks to ultra-fast water transport and anisotropic thermal conductivity causing lesser energy consumption, the rGO-P-FAS membrane got a relatively higher water flux maintaining a stable high salt rejection.

### 3.6. Effects of operating conditions on DCMD performance

The DCMD desalination performance of rGO-P-FAS membrane was further investigated under different feed temperatures (50–80 °C) and SDS concentrations (0.25–0.4 mM) in the feed solution. As shown in Fig. 13a, with the augment of feed temperature, the flux was increased from 23.39 to 82.29 kg m$^{-2}$ h$^{-1}$ while the salt rejection kept at ~99.99%. The increased driving force rising from the higher feed temperature improves the water flux, which proved that MD is indeed a thermally driven process. Furthermore, 0.05 mM SDS was added into the 35 g L$^{-1}$ NaCl feed solution with initial 0.25 mM SDS at 60 °C every 2 h until the SDS concentration reached 0.4 mM. The membrane also showed a stable water flux and salt rejection. This result also demonstrated the excellent chemical and mechanical properties of the rGO-P-FAS membrane, which could be adapted to the feed solution at different temperatures or different SDS concentrations that are often encountered in processing industrial wastewater.

We also evaluated the anti-wetting performance of rGO-P-FAS membrane toward organic pollutants by adding 30 mg L$^{-1}$ humic acid (HA) into the 35 g L$^{-1}$ NaCl feed solution. As shown in Fig. 13b, the excellent salt rejection was maintained during over 180 h of DCMD process, along with a decline of water flux from 56.50 to 36.41 kg m$^{-2}$ h$^{-1}$. HA, one of the organic pollutants, is composed of recalcitrant organic degradation polymer with low to moderate molecular weight, containing both aromatic and aliphatic components with carboxylic and phenolic functional groups [10]. It can absorb or deposit on the surface of the membrane by specific chemical affinity or electrostatic interactions, resulting in the reduction of water passageways [45]. Interestingly, high salt rejection (~100%) of the membrane was maintained...
In summary, an omniphobic rGO membrane was realized by plasma treating GO laminates and then fluoroalkyl grafting. The plasma treatment proved to be crucial in producing a robust low free energy membrane. The resulting omniphobic rGO-P-FAS membrane thus showed a flux of ~35 kg m\(^{-2}\) h\(^{-1}\) and salt rejection of 99.9% under 60 °C for 35 g L\(^{-1}\) NaCl solution with 0.2–0.4 mM SDS during over 450 h continuous DCMD process. This facile plasma-assisted fabrication demonstrated in this work could be a promising approach to develop anti-fouling two-dimensional-material membranes for MD desalination. Besides, the ease of plasma treatment also endows the membrane with good prospects for large-scale application. The industrial application and economic competitiveness of plasma-assisted fabrication largely depend on the membrane performance and stability. Further studies on the performance of GO membranes in practical conditions should be conducted in the future.

**References**


