


## The synthesis of an amended membrane coated with graphene oxide and dopamine & guanidyl based modifier and its antifouling property

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### ABSTRACT

The membrane fouling issue has aroused great concern. To improve the antifouling property, the surface grafting with oxidative deposition were employed to amend PVDF membrane. The modifiers were amino-modified graphene oxide (AMGO), dopamine (DPA) and 1,3-diaminoguanidine hydrochloride (DAGH). To take Bovine Serum Albumin (BSA, 1 g/l) as an example of organic matters, BSA interception rate and pure water flux recovery rate increased to 93.65% and 66.74%, respectively, while the corresponding values for the original membrane were much lower (72.82% and 31.72%). The optimum synthesis conditions were gained as 1.5 mg/ml of DPA, 1 wt% of DAGH, 2 mg/ml of AMGO, 4 h of DPA oxidation deposition time and 1 h of AMGO grafting time. Many functional groups like C = N, -NH<sub>2</sub>, C = O and -OH improved the membrane surface hydrophilicity leading to a higher resistance to organic pollution. Dopamine and guanidyl facilitated the antimicrobial performance of the modified membrane, whose antimicrobial rate was up to 96%, while the raw membrane had no antimicrobial activity. The amended membrane possessed 40% higher mechanical strength than the initial one. It could withstand high pumping suction force. The noteworthy property was that the irreversible fouling rate decreased by 55%. Therefore, the amended membrane could restore its flux much easier.

**Key words:** amino modified graphene oxide, antimicrobial behaviors, dopamine and guanidyl based modifier, flux recovery rate, interception performance, PVDF membrane

### HIGHLIGHTS

- The graphene oxide, dopamine and guanidine-based composite modification offered high hydrophilic and antibacterial radicals.
- The irreversible pollution rate of the modified membrane decreased by 55%, its pure water flux recovery rate increased by twice and BSA interception rate was around 94%.
- The antimicrobial rate of the modified membrane reached 96%, while the original one did not display any antimicrobial behaviors.

### INTRODUCTION

Polyvinylidene fluoride membrane (PVDF membrane) is a type of organic polymeric materials which are widely employed in membrane separation technology. It has outstanding characteristics such as having a simple synthesis process, high strength, low price, etc. PDVF membrane has been frequently employed in the process of filtration and purification of reclaimed water for recycling (Kang & Cao 2014). However, PVDF membrane has possessed weak hydrophobicity and poor anti-fouling property. It is easy to be contaminated during the interception of organics, bacteria and other pollutants in reclaimed water, which causes an increase of transmembrane resistance and a decrease of membrane flux. As a result, the durability of PVDF membrane declines. It then becomes necessary to replace membrane modules frequently to keep the purification efficiency, but the frequent replacement of membrane modules leads to the increase of processing cost (Liu *et al.* 2018). Surface modification is feasible to enhance the anti-fouling performance of PVDF membrane, which can improve the purification efficiency and prolong the service life of membrane modules (Liu *et al.* 2011; Shahkaramipour *et al.* 2017). Currently, there are two main

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directions to improve the anti-fouling property of membranes via surface modification. One is to introduce modifiers with good hydrophilicity to the membrane surface to improve the resistance to organic pollution. For example, it has been proved that graphene oxide (GO) could effectively improve the hydrophilicity of membranes (Choi *et al.* 2013), which weakens the interaction between organic pollutants and membranes, and facilitates the decline of membrane pollution caused by organics as well. Junaidi and coworkers employed GO to modify polyethersulfone (PES) membranes and found that the addition of GO significantly improved the hydrophilicity of the membranes (Junaidi *et al.* 2017). The other is to introduce antimicrobial functional modifiers to the membrane surface to enhance its resistance to bio-fouling. Aryanti and coworkers reviewed the research progress of antibacterial modified membrane in the field of water treatment. The modification methods of polymeric membranes were elaborated in their document, such as blending, grafting and coating (Aryanti *et al.* 2017). Among various antimicrobial modifiers, guanidine antimicrobial agent has attracted much attention with its special antimicrobial property (Zhou *et al.* 2018) of destroying the surface structures of bacteria and other microorganisms. Hence, it becomes hard for microorganisms to propagate on the membrane which leads to an effective resistance to bio-fouling.

The two research directions mentioned above are to improve the antifouling property of membranes solely from the resistance to organic pollution or bio-fouling. However, there are a variety of pollutants in the reclaimed water, including abundant protein organics, oil, bacteria, etc., which require the membranes to possess a higher comprehensive antifouling performance of both organic pollution and bio-pollution. Therefore, it is an ideal method to alleviate bio-fouling of a membrane with a simultaneous modification of hydrophilicity and antibacterial properties. Some researchers have reported different novel approaches to bifunctional membrane modification. For example, Liu and coworkers grafted amphoteric hydrogels to the surface of polyethersulfone (PES) membrane by UV light initiation and then loaded GO on the modified surface of the PES. The results showed that the hydrophilicity and antibacterial properties of the modified membrane were obviously improved. Liu and coworkers synthesized the modifier- quaternary ammonium oxide (QGO) and grafted it on the surface of ultrafiltration membrane by in-situ growth method of quaternary ammonium salt. Afterwards, the bifunctional membrane with hydrophilicity and antibacterial performance was prepared by impregnation phase transformation. It was found that the modified polyvinylidene fluoride (PVDF) membrane had obvious hydrophilicity, antibacterial and mechanical properties compared with the unmodified PVDF membrane (Liu *et al.* 2017; Liu *et al.* 2020). Thus, considering the characteristics of reclaimed water and the current anti-fouling deficiency of modified membranes, we introduce a new promising modified PVDF membrane in this study to tackle the antifouling problems. The new modified membrane has been synthesized through nucleophilic reaction (Zhao *et al.* 2015) by grafting guanidine antimicrobial agent 1,3-diaminoguanidine hydrochloride (DAGH) and AMGO with high hydrophilicity onto PDPA. Here, PDPA, which was formed by oxidative deposition of dopamine (DPA), served as the grafting matrix (Ye *et al.* 2011). Hence, the resistance to organic pollution and bio-pollution of the membrane were simultaneously enhanced. Taking the parameters (DPA concentration, DPA oxidation deposition time, DAGH mass concentration, AMGO concentration and AMGO grafting time) as influence factors, the optimal synthesis conditions of the modified membrane were explored by the orthogonal experimental design and the continuous tests of single factors. To take BSA and escherichia coli as an example of organics and bacteria in reclaimed water respectively, the interception capacity and antifouling property of the modified membrane were investigated by testing its selective permeability, the resistance to organic pollution, stability and long-lasting antimicrobial performance at the optimal synthesis conditions.

## MATERIALS AND METHODS

### Experimental materials

The original polyvinylidene fluoride membrane (PVDF membrane) with area of 36.3 cm<sup>2</sup> was supplied by Shanghai Snape Membrane Separation Technology Co., Ltd Amino modified graphene oxide (AMGO), with thickness of 1.2 nm–1.6 nm, purity of 99 wt% (mass percentage concentration), was produced locally in the laboratory (Guangdong University of Technology, China). Chemicals dopamine (DPA) and 1,3-diaminoguanidine hydrochloride (DAGH) with purity of 97 wt% (mass percentage concentration) were obtained from Shanghai Aladdin Biochemical Technology Co. Ltd As for the biological reagents, tris hydroxy methyl aminomethane (Tris, molecular weight: 121.14) was purchased from Sinopharm Chemical Reagent Co., Ltd; bovine serum albumin (BSA, Aladdin) was bought from Shanghai Aladdin Biochemical Technology Co. Ltd; escherichia coli strains (ATCC25922, molecular weight: 66.446 KDa) were offered by Shanghai Luwei Technology Co., Ltd; luria-bertani (LB) medium was provided by Haibo Biotechnology. For analytical reagents, hydrochloric acid (HCl, molecular weight: 36.5) and absolute alcohol (C<sub>2</sub>H<sub>6</sub>O, molecular weight: 46.07) were provided by Sinopharm Chemical

Reagent Co., Ltd; sodium chloride (NaCl, molecular weight: 58.44), disodium hydrogen phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , molecular weight: 358.14), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , molecular weight: 136.09) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd

### Synthesis procedure of the modified membrane

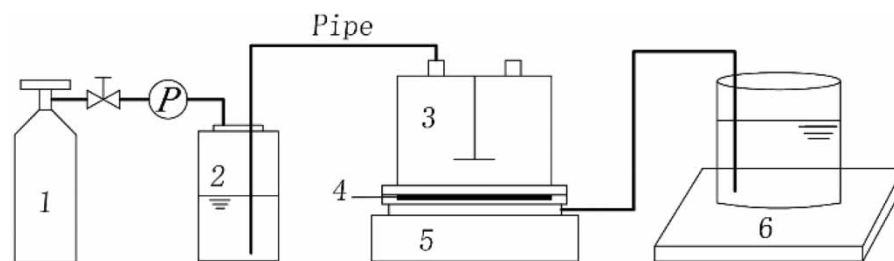
This section illustrated the synthesis procedure of the modified membrane. First of all, the original PVDF membrane module was pretreated and activated by soaking in absolute ethanol for 30 min completely, and then immersing in ultrapure water for 30 min to replace the ethanol fully and restore the original membrane flux. Afterwards, the reaction solution was made by adding DPA and DAGH into Tris-HCl buffer solution ( $\text{pH} = 8.5$ ). Then, the membrane, of which flux was restored, was soaked in the reaction solution for water bath reaction (at  $25^\circ\text{C}$ ), where several important reactions happened. The possible reactions were as follows, DPA could be oxidized and deposited to produce polydopamine (PDPA). The amino groups on the DAGH could be compounded with PDPA through nucleophilic reaction via the amino groups to form a layer of modifier (PDPA-DAGH) on the membrane, then the PDPA-DAGH modified membrane was ready. Finally, the intermediate PDPA-DAGH modified membrane was immersed in the AMGO reaction solution for further grafting modification. The compound modified layer was formed on the surface of the membrane and the composite modified membrane was synthesized completely.

### The experimental device

In order to evaluate the anti-fouling performance of the modified membrane, a test device was designed as shown in Figure 1 with the initial concentration of BSA solution was 1 g/l. Before the modified membrane went through testing in the device, its pure water flux was measured with pure water as the untreated water reference. The membrane was placed in a dead-end filtration device (see Figure 1) with 0.15 Mpa of pressure for 30 min of preloading at room temperature. Then, the pure water flux was tested at 0.10 MPa for 10 min by gravimetric method. Afterwards, pure water in the ultrafiltration cup was replaced with BSA solution. The initial concentration of BSA solution 1 g/l was added into the ultrafiltration cup, filtered and sampled at 0.1 MPa for 60 min. Then, the absorbance of BSA solution was measured before and after filtration by ultraviolet (UV) spectrophotometer (UV5100, Shanghai Yuanshi Instrument Co., Ltd., 2016). Lastly, the BSA interception rate ( $\eta$ ) of the membrane was calculated and the corresponding membrane flux  $J_{\text{BSA}}$  was recorded. Therefore, the anti-pollution performance of the membrane was explored according to the BSA interception rate.

### Orthogonal test design on the determination of the optimal synthesis conditions

The synthesis conditions had an important impact on the desiring antifouling performance of the modified membrane. The orthogonal test design method was adopted to determine the optimum synthesis conditions. In the orthogonal test design,  $L_n(f^m)$  was used to represent the effects of various factors, where  $f$  and  $m$  denote the number of levels and factors, respectively, and  $n$  denotes the total number of experiments at different test conditions. The factors of the synthesis experiments included DPA concentration ( $C_{\text{DPA}}$ ), DPA oxidation deposition time ( $t_{\text{DPA}}$ ), DAGH mass concentration ( $C_{\text{DAGH}}$ ), AMGO



Note: 1- Nitrogen gas bottle    4- The modified membrane  
 2- The buffer bottle        5- Magnetic stirrer  
 3- Ultrafiltration cup      6- Electronic balance

**Figure 1** | Dead end filtering device.

concentration ( $C_{AMGO}$ ) and AMGO grafting time ( $t_{AMGO}$ ). Four levels were set for each factor. The evaluation index- flux recovery rate of pure water ( $FRR$ ) was employed in the orthogonal test design. Here  $FRR$  was the key index to characterize the antifouling performance of the membrane.

The orthogonal test design consisted of several steps. First, a standard orthogonal test design table was selected. The 'factor' columns of the table were filled with their own levels. Next, experiments were conducted according to the orthogonal test design scheme. The test results were entered into the 'index' column in the  $L_n(f^m)$  format. Then, the sum ( $S$ ) of each index value corresponding to the same level of each factor column was calculated. In addition, the average values of 'K' were gained through 'S' which were divided by the number of occurrences in each level. Finally, the extremum 'R' value, the difference between the maximum and minimum values of 'K', was determined. 'K' was applied to denote the optimum combination of factors corresponding to the optimal experimental conditions, and 'R' was used to evaluate the degree of influence of each factor on the antifouling properties of the modified membrane in the synthesis process. Higher values of 'R' were associated with higher levels of influence on an index.

Hence, the influence degree of each factor on the antifouling performance of the modified membrane was evaluated based on the value of 'R', and the optimum synthesis conditions of the modified membrane were determined accordingly.

## Anti-fouling performance tests of the modified membrane

### Selective permeability

The selective permeability of the modified membrane was evaluated comprehensively by pure water flux  $J_{BSA}$  and the interception rate ( $\eta$ ) of organic pollutants (Zhang *et al.* 2020). The experimental procedure and tests methods were similar to those in the section 'The experimental device'.

### Resistance to organic pollution

Pure water flux recovery rate ( $FRR$ ), total pollution rate ( $R_t$ ), reversible pollution rate ( $R_r$ ), and irreversible pollution rate ( $R_{ir}$ ) were employed as four indexes for analyzing membrane fouling, which can reflect the antifouling property of the membrane. After the determination of  $J_{BSA}$  according to the method mentioned in the section 'The experimental device', the BSA contaminated membrane was cleansed by a crossflow method, and the pure water flux of the cleansed membrane was measured and recorded as  $J_{rec}$ . Therefore, the indexes representing membrane pollution were calculated. For example,  $FRR$ ,  $R_t$ ,  $R_r$ ,  $R_{ir}$  were the ratios of  $J_{rec}$ ,  $J_{rec} - J_{BSA}$ ,  $J_0 - J_{BSA}$ ,  $J_{rec} - J_{BSA}$  to  $J_0$  respectively, where  $J_0$  stood for initial pure water flux of the membrane;  $J_{BSA}$  meant the flux of BSA solution after membrane filtration for 60 min;  $J_{rec}$  represents pure water flux of membrane after cross-flow cleansing.

### Stability of the resistance to organic pollution

After the first measurement of  $J_0$ ,  $J_{BSA}$ ,  $J_{rec}$ , the second  $J_{BSA}$  and  $J_{rec}$  were obtained by conducting the filtration of the BSA solution through the first cleansed membrane. The polluted membrane was cleansed by the crossflow method again. In the same manner, the rest of three filtration- cleansing cycles were conducted. Thus the stability of the resistance to organic pollution of the modified membrane was investigated. During the tests, real-time flux data were read with 5-min intervals to prepare for depicting the normalized flux curve. The normalized flux is the ratio of the real-time flux to the initial pure water flux  $J_0$ .

### Antimicrobial performance

To take escherichia coli as an example, the antimicrobial performance of the membrane was explored according to the colony forming units on Luria-Bertan (LB) solid medium based on the dilution spread plate method. First, the strains were cultured in LB medium until a stable stage ( $1 \times 10^9$  cfu/ml) which represented the bacterial stable period (Liu *et al.* 2007), and then the bacteria suspensions were diluted by 10, 100 and 1,000 times respectively. At the same time, the cultivation medium, culture dish, normal saline, pipette gun head and coating rod were put into the high-pressure sterilizer for 30 min at the pressure of 0.142 Mpa and the temperature of 121°C.

Next, 100  $\mu$ L of the bacteria suspension ( $1 \times 10^6$  cfu/ml) was evenly spread on the surface of the sterilized membrane in the test group, before putting the membrane in a sterile culture dish. The dish with the membrane was sealed up, and placed in a constant temperature incubator for 2 h at 38°C. After the cultivation, the bacterial suspension on the membrane was rinsed with normal saline. 100  $\mu$ L of rinsing liquid was drawn and evenly spread on LB solid medium. Then this LB solid medium was cultured for 18 h at constant temperature (38°C). The colony forming units on the medium were counted (noted as 'A'). The bacterial suspension of the blank contrast group did not contact the membrane and was directly spread on the glass slide for cultivation. Other experimental steps and operations were the same as those of the test group where the bacterial

suspension was spread on the membrane. Finally, the colony forming units on the medium of the blank group were numbered (noted as 'B'). After the first antimicrobial test, the membrane was cleansed by a crossflow method. The above steps were then repeated for a total of four antimicrobial tests. The antimicrobial rate 'M' was the ratio of B-A to B. Here, A is the colony forming units in the test group with the bacterial suspension spread on the membrane; B is the colony forming units in the blank contrast group with the bacterial suspension coated on the glass slide without contacting the membrane.

## RESULTS AND DISCUSSION

### The determination of the optimum synthesis conditions of the modified membrane

The orthogonal test design was conducive to determining the optimum synthesis conditions of the modified membrane. Five factors were selected below: DPA concentration ( $C_{DPA}$ ), DPA oxidation deposition time ( $t_{DPA}$ ), DAGH mass concentration ( $C_{DAGH}$ ), AMGO concentration ( $C_{AMGO}$ ), and AMGO grafting time ( $t_{AMGO}$ ). Four levels were set for each factor. According to the extremum R, the influence degree of each factor on the antifouling performance was evaluated, which illustrated the optimal synthesis conditions of the modified membrane.

### Effect of synthesis conditions on antifouling performance

The orthogonal experimental results of the synthesis conditions on antifouling performance were shown in Table 1. The optimum synthesis conditions were determined based on the index- flux recovery rate of pure water (FRR). Higher values of R were associated with higher levels of influence on an index. For the five factors mentioned above, their corresponding R

**Table 1** | The orthogonal experimental design and the analysis results

The sequence of the test	Influencing factors					Flux recovery rate FRR (%)
	$C_{DPA}$ (mg/ml)	$C_{AMGO}$ (mg/ml)	$C_{DAGH}$ (wt%)	$t_{DPA}$ (h)	$t_{AMGO}$ (h)	
1	1	0.5	0.5	2	1	38.13
2	1	1	1	4	2	46.92
3	1	2	1.5	6	3	42.85
4	1	3	2	8	4	35.09
5	1.5	2	1	2	4	56.43
6	1.5	3	0.5	4	3	61.32
7	1.5	0.5	2	6	2	42.38
8	1.5	1	1.5	8	1	43.51
9	2	3	1.5	2	2	49.46
10	2	2	2	4	1	54.18
11	2	1	0.5	6	4	45.45
12	2	0.5	1	8	3	36.12
13	2.5	1	2	2	3	37.47
14	2.5	0.5	1.5	4	4	38.63
15	2.5	3	1	6	1	50.26
16	2.5	2	0.5	8	2	47.59
the original membrane						30.51
$K_1$	40.75%	38.82%	48.12%	45.37%	46.52%	
$K_2$	50.91%	43.34%	47.43%	50.26%	46.59%	
$K_3$	46.30%	50.26%	43.61%	45.24%	44.44%	
$K_4$	43.49%	49.03%	42.28%	40.58%	43.90%	
$i_{max}$	1.5 mg/ml	2 mg/ml	0.5 wt%	4 h	2 h	
R	10.16%	11.45%	5.84%	9.69%	2.69%	

Note: The subscripts 1, 2, 3 and 4 of K are used to indicate the first, second, third and fourth levels of each factor.  $K_i$  refers to the arithmetic mean value of FRR of all tests when the factors in this column are at the  $i$ -th level;  $i_{max}$  is the optimal level, which refers to the level corresponding to the maximum value of  $K_1$ - $K_4$ ; R indicates the extreme value of  $K_1$ - $K_4$ .

values were ranked in the sequence below (see in Table 1),  $R-C_{AMGO} > R-C_{DPA} > R-t_{DPA} > R-C_{DAGH} > R-t_{AMGO}$ . It revealed that AMGO concentration ( $C_{AMGO}$ ) has the strongest influence on the flux recovery rate and antifouling properties of the modified membrane among the five factors, then followed  $C_{DPA}$ ,  $t_{DPA}$  and  $C_{DAGH}$ , while AMGO grafting time ( $t_{AMGO}$ ) has the minimum impact. Therefore, the influence degree of each factor on FRR was ranked as that  $C_{AMGO} > C_{DPA} > t_{DPA} > C_{DAGH} > t_{AMGO}$ . In addition,  $R-C_{AMGO}$ ,  $R-C_{DPA}$  and  $R-t_{DPA}$  were significantly higher than  $R-C_{DAGH}$  and  $R-t_{AMGO}$ , which disclosed that  $C_{AMGO}$ ,  $C_{DPA}$  and  $t_{DPA}$  were the key factors influencing the antifouling properties of the membrane. 'K' was applied to represent the optimum combination of factors corresponding to the optimal synthesis conditions. A smaller value of K was connected with a lower level of impact on an index. As shown in Table 1, the optimal levels of the three factors ( $C_{AMGO}$ ,  $C_{DPA}$  and  $t_{DPA}$ ) in the orthogonal test was  $C_{AMGO}$  2 mg/ml,  $C_{DPA}$  1.5 mg/ml and  $t_{DPA}$  4 h corresponding to their maximum K value respectively. The influences of the other two factors  $C_{DAGH}$  and  $t_{AMGO}$ , were more complicated. According to the K value of the factor  $C_{DAGH}$ , the optimal concentration of  $C_{DAGH}$  matched with the lowest level (0.5 wt%), but the real situation is that excessively low value of  $C_{DAGH}$  may cause the negative antimicrobial performance of the modified membrane (Ding 2017). Moreover, long-lasting run would result in serious biofilm pollution at the condition of low value of  $C_{DAGH}$ . Therefore, continuous experiments with single factor  $C_{DAGH}$  was designed to display its impact on the antimicrobial performance of the modified membranes further. In addition, the maximum K value of the factor  $t_{AMGO}$  showed its optimal grafting time as 2 h. However, the first and the second biggest K values ( $K_1 = 46.52\%$  and  $K_2 = 46.59\%$ ) were close at  $t_{AMGO}$  2 and 1 h respectively, which led to a similar antifouling performance. Therefore,  $t_{AMGO} = 1$  h was selected as the optimal grafting time of AMGO.

#### Effect of $C_{DAGH}$ on antimicrobial properties of the modified membrane

$C_{DAGH}$  is the key factor because the guanidine group of DAGH dominated the antimicrobial property of the modified membrane. Based on the optimal DAGH concentration determined by orthogonal test, continuous experiments were designed to explore the effect of different  $C_{DAGH}$  on the antimicrobial property. Figure 2 shows the antimicrobial test results of the modified membrane when  $C_{DAGH}$  was 0.3 wt%, 0.5 wt%, 0.7 wt%, 1.0 wt% and 1.5 wt% respectively. The corresponding antimicrobial rate was  $(31.8 \pm 3.8)\%$ ,  $(61.3 \pm 4.3)\%$ ,  $(85.3 \pm 2.2)\%$ ,  $(91.6 \pm 3.7)\%$  and  $(92.1 \pm 3.0)\%$ . With the increase of  $C_{DAGH}$ , the antimicrobial property of the modified membrane went up. When  $C_{DAGH} = 1.0$  wt%, the antimicrobial rate was close to that of  $C_{DAGH} = 1.5$  wt%, both of which were significantly higher than that of  $C_{DAGH} = 0.5$  wt%. Meanwhile, from Table 1,  $K_2$  with  $C_{DAGH} = 1.0$  wt% was close to  $K_1$  with the optimal concentration  $C_{DAGH} = 0.5$  wt%, both of them were obviously higher than that of  $K_3$  with  $C_{DAGH} = 1.5$  wt%. This revealed that the modified membrane with  $C_{DAGH}$

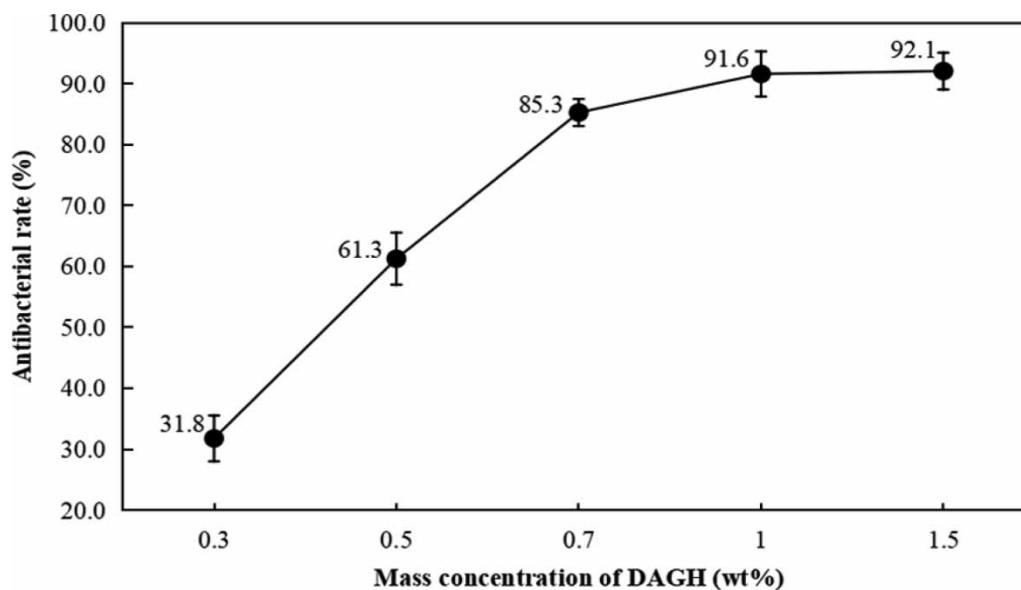


Figure 2 | The antimicrobial rate of the amended membrane at different mass concentration of DAGH.

1.0 wt% has owned a better resistance to organic pollution and a stronger antimicrobial performance than the ones with 0.5 wt% and 1.5 wt%. Therefore,  $C_{\text{DAGH}} = 1.0 \text{ wt\%}$  was selected as the optimal DAGH mass concentration.

In conclusion, the optimal synthesis conditions of the modified membrane were determined as that  $C_{\text{DPA}} = 1.5 \text{ mg/ml}$ ,  $t_{\text{DPA}} = 4 \text{ h}$ ,  $C_{\text{DAGH}} = 1.0 \text{ wt\%}$ ,  $C_{\text{AMGO}} = 2 \text{ mg/ml}$ ,  $t_{\text{AMGO}} = 1 \text{ h}$  when both the resistance to organic pollution and antimicrobial properties of the membrane were considered at the same time.

## The characterization of the modified membrane

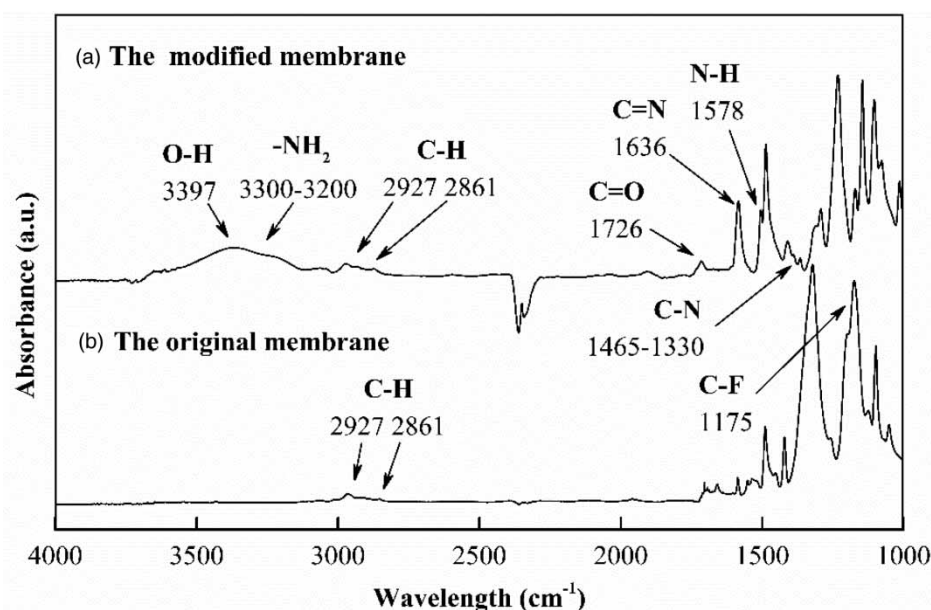
### Chemical functional group analysis and the vibration adsorption peak characteristics

The infrared spectra characteristics of the original membrane and the modified one were displayed in Figure 3. It was very clear that the nano-modifying agents AMGO, PDPA and DAGH have contributed a great many polar groups attached on the surface of the modified membrane, like -OH, C=O, -NH<sub>2</sub>, N-H and C=N. Therefore, the hydrophilic nature and the anti-fouling performance were improved significantly.

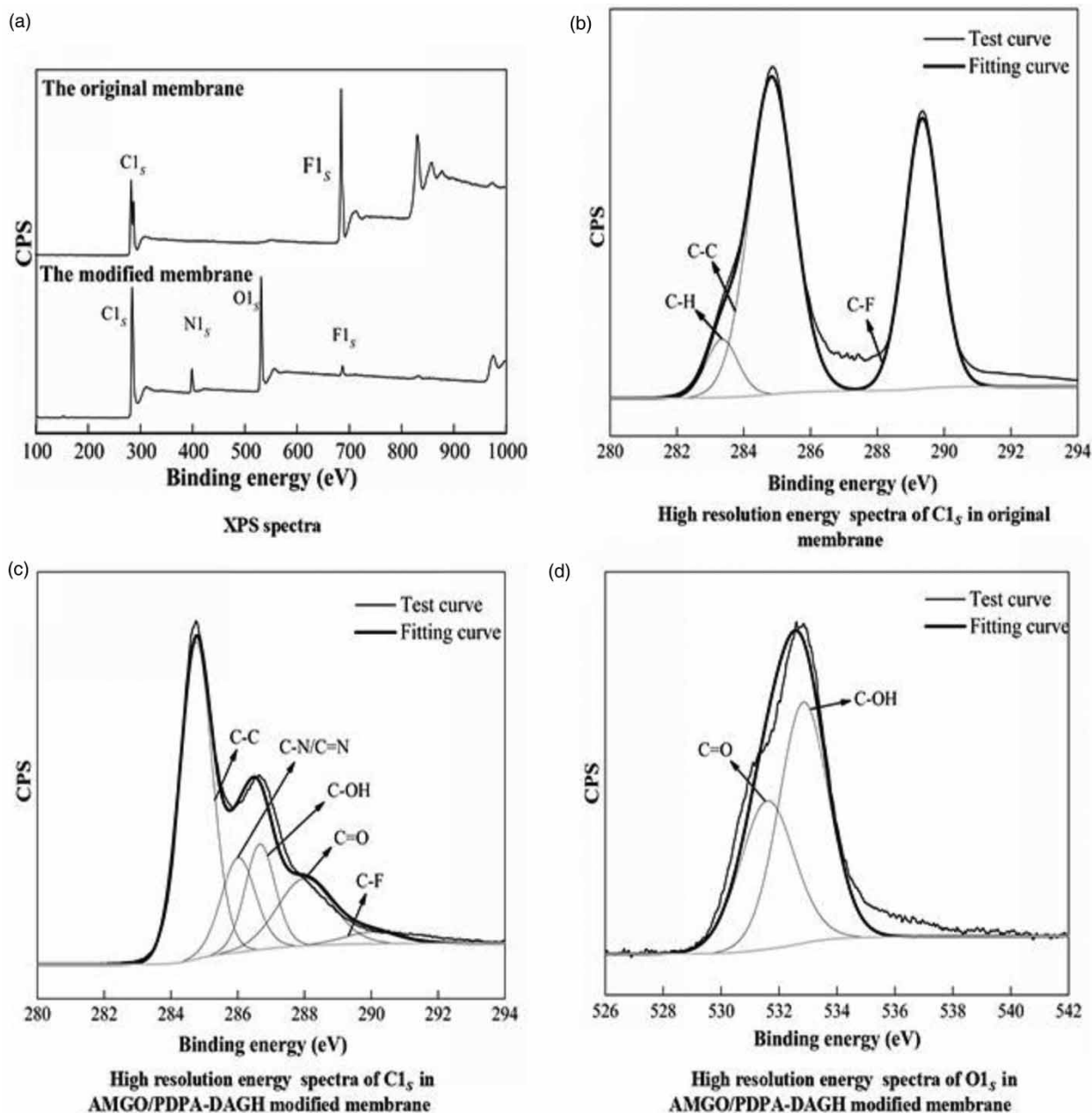
The properties of the polar groups and the vibration adsorption peak characterized by Fourier transform infrared spectrometer (FTIR, Nicolet IS50, Thermo Fisher, 2016) were illustrated as below according to Figure 3. The position near  $1,176 \text{ cm}^{-1}$  corresponded to the vibration adsorption peak of the C-F bond in PVDF materials; the stretch vibration adsorption peak of the hydroxyl groups (C-H) was in line with the position of  $2,861 \text{ cm}^{-1}$  and  $2,927 \text{ cm}^{-1}$  which was consistent with the characteristic absorption peaks of PVDF in literature (Shao *et al.* 2014).

Compared with the original PVDF membrane (Figure 3(b)), the modified one manifested strong vibration adsorption peaks at  $3,397 \text{ cm}^{-1}$  and  $1,726 \text{ cm}^{-1}$  corresponding to the phenolic hydroxyl bond (-OH) and quinone carbonyl bond (C=O) produced in the process of the oxidation and deposition of dopamine to form PDPA (Chang 2014) (Figure 3(a)); strengths of vibration peaks at  $3,200\text{--}3,300 \text{ cm}^{-1}$ ,  $1,636 \text{ cm}^{-1}$  and  $1,578 \text{ cm}^{-1}$  were enhanced. This proved that AMGO introduced many polar groups such as -NH<sub>2</sub>, C=N, N-H to the surface of the modified membrane. The nucleophilic reaction happened between the functional group -NH<sub>2</sub> carried by DAGH and AMGO with phenolic hydroxyl carried by PDPA. Then -NH<sub>2</sub> could be grafted onto PDPA. Hence, some of the hydrophilic properties were contributed by N-H and C=O. The noteworthy part was that the antimicrobial guanidine group was successfully grafted onto the membrane surface because polar group C=N can be detected.

XPS spectra displayed the facts to confirm the modified layer was successfully attached to the surface of PVDF original membrane further (see Figure 4). The modifier introduced elements Oxygen (O) and Nitrogen (N) into the membrane surface.



**Figure 3** | FTIR spectra for the modified membrane (a) and the original one (b).



**Figure 4** | XPS spectra of the modified membrane and the original one.

In the full spectrum of the modified membrane, new  $N_{1s}$  and  $O_{1s}$  characteristic peaks appeared at 399 eV and 533 eV (see Figure 4(a)) (Sui 2012) except the  $Cl_{1s}$  and  $F_{1s}$  characteristic peaks of the original membrane at 285 eV and 687 eV. When the surface of the original membrane was coated with the modifiers, the intensity of the  $F_{1s}$  characteristic peak decreased conspicuously. On the surface of the modified membrane, there were not only C-C bonds and C-F bonds from the original one (see Figure 4(b)), but also new characteristic peaks of chemical functional groups like C-N/C=N, C-OH and C=O bonds at 285.9 eV, 286.5 eV and 288.0 eV respectively (see Figure 4(c)), and C=O and C-OH bonds at 531.7 eV and 532.8 eV separately (see Figure 4(d)) (Li *et al.* 2012). The X-ray photoelectron spectrometer (XPS, Escalab 250Xi, Thermo Fisher, 2016) characterization results of the membranes were consistent with those from FTIR characterization. Therefore, it was clear that the modified layer was successfully attached to the surface of PVDF original membrane, and was conducive to produce a modified membrane with enhanced hydrophilic properties and antifouling performance compared to the original one.



### Static contact angle

Static contact angle, tested by video optical contact angle measuring instrument (OCA100, Dataphysics, 2015), is the most frequently used index for characterizing hydrophilic properties of membranes. The static contact angle of the modified surface ( $30.2^\circ$ ) was decreased by 43.9% of that of the original one ( $68.7^\circ$ ) after introducing the highly hydrophilic AMGO as the modifying agents. The hydrophilicity of the modified membrane was enhanced markedly. The pure water flux of the modified membrane ( $534.31 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) negligibly dropped compared with that of the original one ( $560.92 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) after modification even though the introduction of the modifier on the membrane surface causing the pore size to be slightly reduced. The improvement of the hydrophilicity can partially offset pure water flux loss. It indirectly proved that antifouling performance of the modified membrane was greatly improved as well. Therefore, lower static contact angle can be employed to reveal the enhancement of the hydrophilic property and antifouling performance of the modified membrane.

### Morphological features and elemental spectrum analysis

The surface morphological features of the original membrane and the modified one were explored by Field-emission scanning electron microscope (FESEM, SU8220, Hitach, 2017) and atomic force microscope (AFM, Dimension FastScan, Bruker, 2016) (see Figures 5 and 6). The original membrane surface was uneven and full of many dense pores. Its texture was relatively loose and rough (see Figure 5(a) and 5(b)), which may be one of the features influencing its mechanical strength (Zhao 2015). After the intermediate PDPA-DAGH modified layer was embedded on the surface of the original membrane, the surface appearance of the PDPA-DAGH modified one has become flat and smooth (see Figure 5(c)). What's more, the subsequent grafted AMGO was laminated on the surface of the PDPA-DAGH modified layer, the modified membrane surface was displayed flat and its structure was compact and strong (see Figure 5(d)).

AFM was used to further clarify the membrane surface roughness and flatness characteristics (see Figure 6). The surface roughness corresponding to the original membrane and the modified one was  $R_a = 46.5 \text{ nm}$  and  $R_a = 18.3 \text{ nm}$  respectively. The surface roughness of the modified membrane decreased significantly and was smoother than that of the original one. The characterization resulting from AFM were consistent with that from FESEM. Surface roughness would affect the flow characteristics of the membrane surface. Smooth and flat membrane surface weakened the attachment and accumulation of proteins and other organic pollutants on the membrane and reduced the probability of bacterial reproduction (Peng *et al.* 2004), which was conducive to improving the antifouling property of membrane surface.

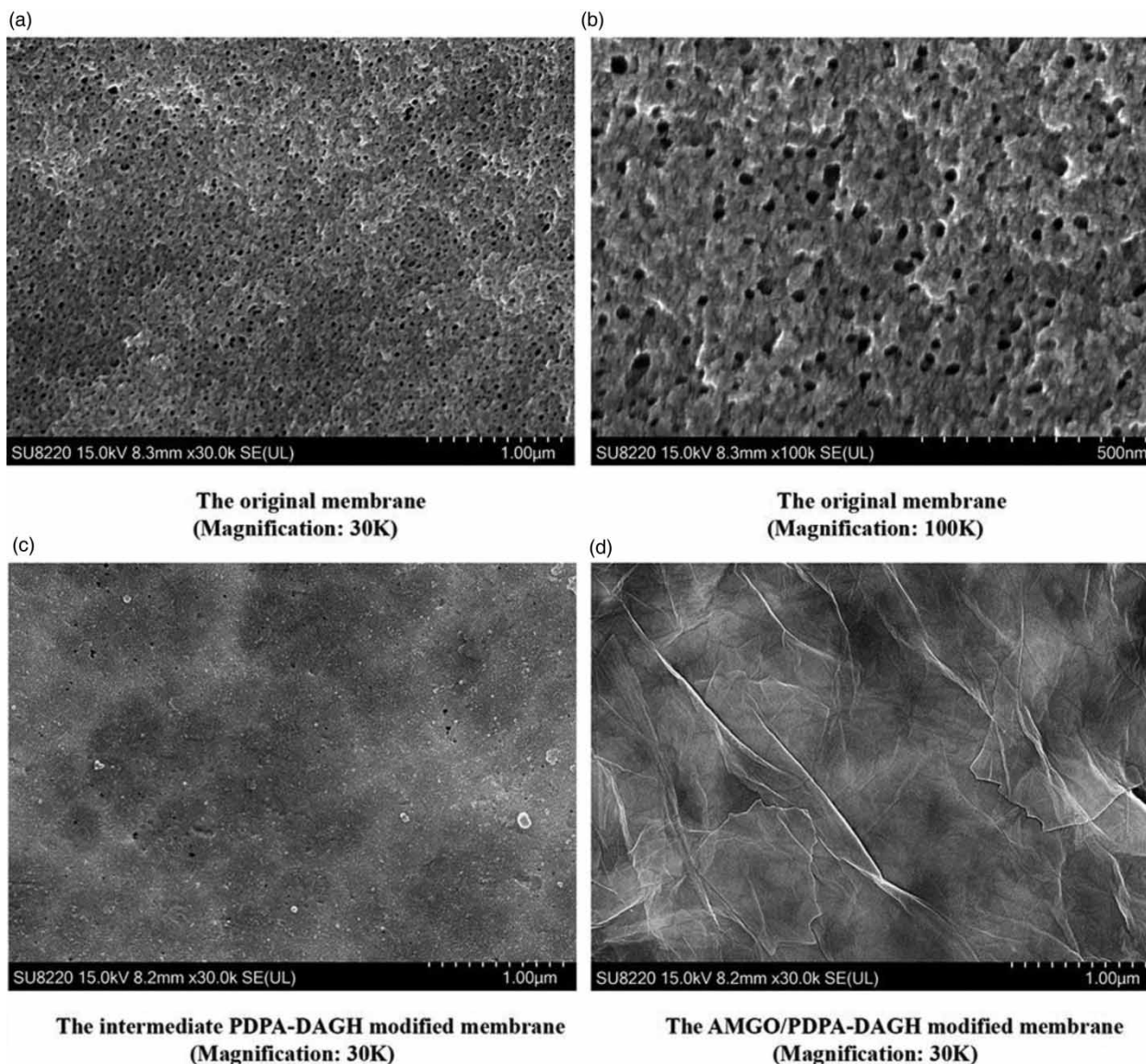
### Mechanical strength

Mechanical strength is the key index of membrane durability which can be measured by electronic universal testing machine (Inspekt Table Blue, Hegewald & Peschke, 2017). The test results were shown that, the width and thickness of the membrane remained the same after and before modification; the tensile strength of the modified membrane was 22.83 Mpa, around 40% higher than that of the original one (16.34 Mpa); the Young's modulus of the modified membrane increased from 331.30 Mpa (for the original membrane) to 376.24 Mpa. For the original membrane, its pore structure was loose and the roughness was high (see Figures 5(a) and 6(a)). The uneven part was the blind area of stress transfer, which made the loads unable to be effectively and evenly delivered and resulted in the poor mechanical strength of the original membrane. However, the modified layer was filled in the uneven area and firmly bound to the membrane surface, so that the load could be effectively and evenly transferred. Therefore, the mechanical strength of the modified membrane was effectively improved.

### Antifouling performance

#### Selective permeability and the resistance to organic pollution

Compared with the corresponding performance parameters of the original membrane and the modified one, the BSA interception rate ( $\eta$ ) of the former was 72.82%, while the latter increased to 93.65%, which demonstrated that the modified membrane has possessed better selective permeability; the pure water flux recovery rate of the former was 31.72%, the latter was 66.74% instead; the total pollution rate reduced from 77.26% (for the former) to 56.43% (for the latter). It should be noted that the irreversible fouling rate of the modified membrane (31.22%) decreased by 55% compared with that (69.44%) of the original one. The reason was that the decrease of surface roughness weakened the interaction between the modified membrane and organic pollutants, which facilitated the organic pollutants trapped on the surface to be removed effectively by cross-flow cleansing. In addition, the surface of the modified membrane has possessed good hydrophilicity and high free energy. According to the minimum energy principle, when water contacted with the membrane, the water with

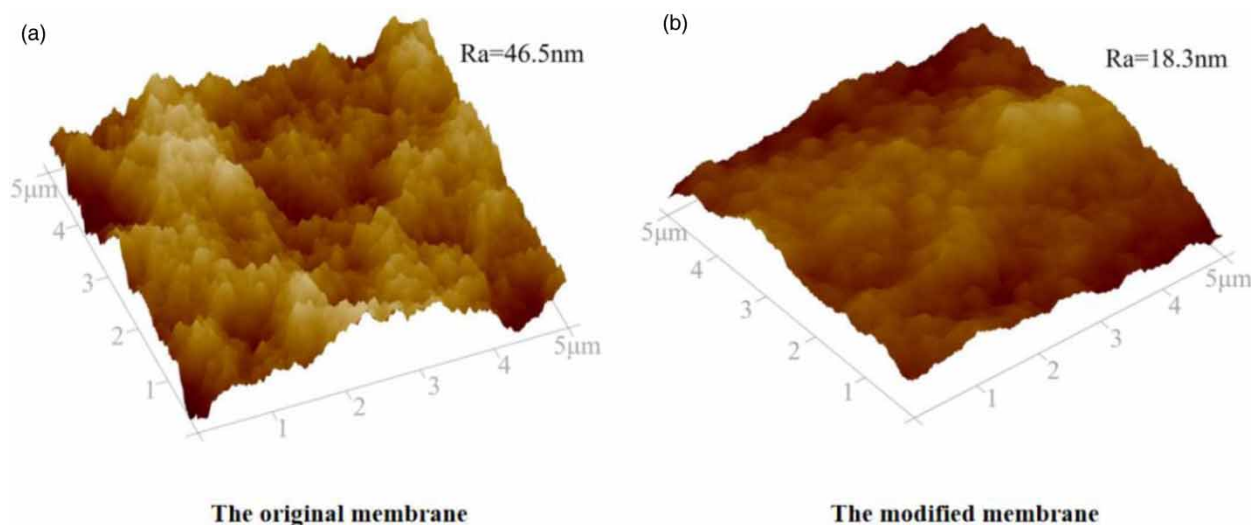


**Figure 5** | FESEM images of membrane surface features and its morphological structure.

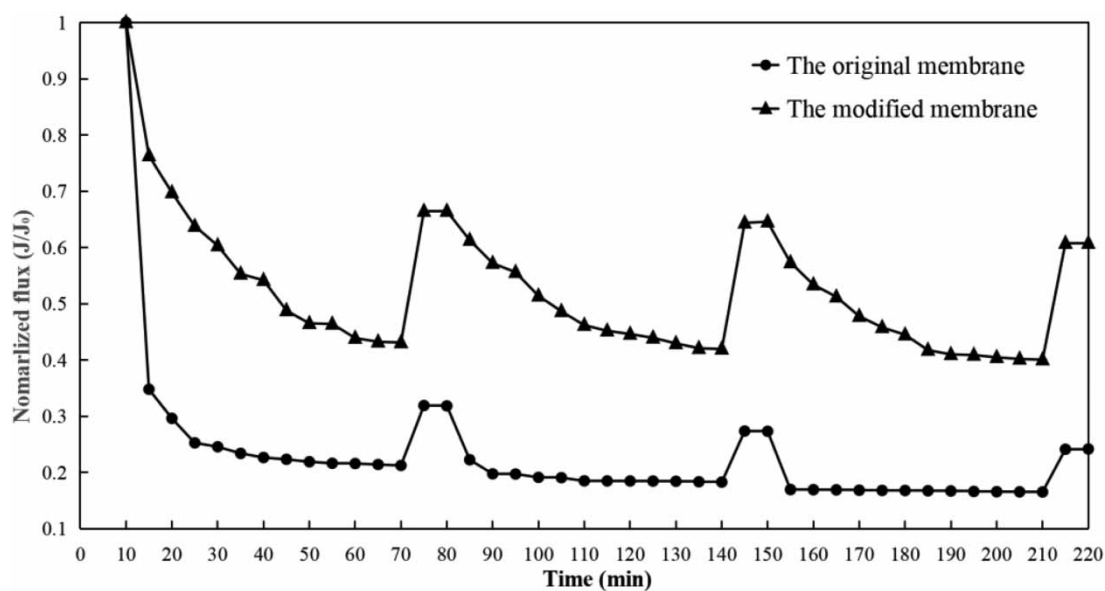
lower surface free energy was easier to be spread and permeated on the membrane than the one with higher surface free energy, which optimized the whole energy system (Wang 2017). The optimal energy system could weaken the adhesive power of hydrophobic pollutants to the membrane, and reduce the entropy loss. Thus, the resistance to organic pollution of the modified membrane has been significantly improved. The water flux of the modified membrane was slightly lower than that of the original one due to the firm adhesion of the modifier on its surface, but other properties, like hydrophilicity and free energy were remarkably boosted, which was leading to a favourable interception performance and antifouling behaviors.

#### Stability of the resistance to organic pollution

For the modified membrane, its stability of the resistance to organic pollution was explored through multiple cycles of the filtration- cleansing taking BSA as a pollutant. The results are shown in Figure 7. The water flux of the original membrane declined rapidly with the addition of BSA solution due to the formation of membrane pollution. After the first cycle of filtration -cleansing, the initial pure water flux of the original membrane and the modified one in the second purification



**Figure 6** | AFM 3D image of membrane surface features and its morphological structure.



**Figure 7** | Normalized flux in four consecutive filtration- cleansing cycles.

round dropped 69.1% and 33.5%, respectively. The normalized flux curve (the ratio of the real-time flux to the initial pure water flux  $J_0$ ) lowered down to 0.32 and 0.67 accordingly. After the first round of membrane filtration, the cross-flow cleansing could not effectively remove the adhered contaminants on the surface of the original membrane. Its normalized flux curve of filtration-cleansing cycle has had a clear period of the adsorption-desorption equilibrium while that of the modified membrane was not obvious, which indicated that the modified membrane has owned a stronger buffering capacity on BSA pollution. After three filtration – cleansing cycles were completed, the flux recovery rate of the modified membrane was still as high as 60.76%, which presented that the modified layer on the membrane surface did not fall off with cross-flow cleansing and had stable and durable resistance to organic pollution. This resistance to organic pollution was related to the improvement of mechanical strength of the modified membrane. The decrease of surface roughness changed the flow state on the membrane surface, reduced the probability of turbulence shock, and extended the service life of the modified membrane. In conclusion, compared with PVDF original one, the modified membrane has possessed a stronger resistance to organic pollution and a more stable performance. It can be reused after cross-flow cleansing.

### Long lasting antimicrobial behaviors

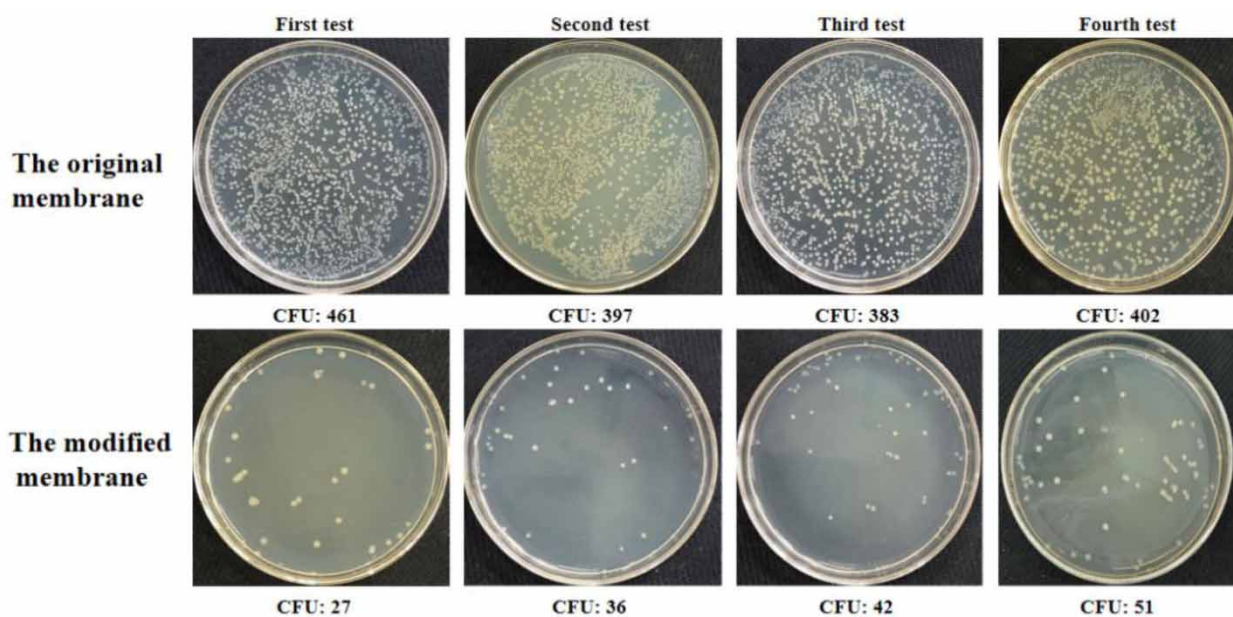
The colony growth numbers and its statistical quantity representing the long-lasting antimicrobial behaviors were shown in Figure 8. The original PVDF membrane is a chemically stable polymer possessed with strong polarity of carbon and fluorine bonds in its molecular chain, so it has strong chlorine tolerance (Song 2011). However, the chlorine tolerance of the original membrane was weak to microbial growth control because the colony growth numbers and its statistical quantity representing the long lasting antimicrobial behaviors were very high. The amended membrane being coated with graphene oxide and dopamine & guanidyl based modifier has possessed a high antimicrobial performance. The antimicrobial rates of the amended membrane were  $(92.3 \pm 3.7)\%$ ,  $(88.5 \pm 2.9)\%$ ,  $(87.9 \pm 3.3)\%$  and  $(85.6 \pm 3.6)\%$  when going through four consecutive tests (contact for 2 h at 38 °C), respectively. Guanidine group in the modifier DAGH contributed to the high antimicrobial performance. The positively charged cationic guanidine group can adsorb bacteria by electrostatic attraction, and combine with the negative potential point of the cell membrane, which resulted in the imbalance of the charge distribution, destroyed the surface structure of bacteria, and then killed them (Li *et al.* 2014; Sun *et al.* 2018). The modifier AMGO in the outer layer of the modified membrane has played a role in keeping DAGH on the surface of the membrane, reduced the desorption rate of DAGH and thus maintaining the antimicrobial rate at a high level (85.6%) after repeated four cycles of filtration-cleansing. Compared with the original PVDF membrane without antimicrobial property, the modified one has a stronger antimicrobial performance and could play a lasting antimicrobial role in the continuous filtration-cleansing runs.

### CONCLUSION

A promising modified membrane was achieved by coating with modifiers such as amino modified graphene oxide (AMGO), dopamine (DPA) and 1,3-diaminoguanidine hydrochloride (DAGH) by taking surface grafting coupled with the oxidative deposition as the modification methods.

Priority ranking of the influencing factors on the synthesis of amended membrane concluded that,  $C_{AMGO}$ ,  $C_{DPA}$  and  $t_{DPA}$  were the key factors affecting the anti-pollution performance of the membrane;  $C_{AMGO}$  was the dominant factor, followed by  $C_{DPA}$  and  $t_{DPA}$ , and  $t_{AMGO}$  has had the least influence.

Under the optimal synthesis conditions with 1.5 mg/ml of DPA, 1 wt% of DAGH, 2 mg/ml of AMGO, 4 h of DPA oxidation deposition time and 1 h of AMGO grafting time, the interception performance and antimicrobial behaviors of the modified membrane were enhanced remarkably. The modifiers introduced hydrophilic functional groups such as C=N, -NH<sub>2</sub>, C=O and -OH to the membrane surface, and the static contact angle of the modified membrane decreased by 43.9%. The modified layer enhanced the mechanical strength of the membrane because its tensile strength was around



**Figure 8** | The number of colony forming units (CFU) in the four continuous filtration-cleansing runs.

40% higher than that of its initial data. Compared with the surface roughness of the original membrane (46.5 nm), that of the modified one (18.3 nm) dropped by 60.7%, which improved the stress transferring dead zone on the membrane surface. The BSA interception rate and pure water flux recovery rate of the modified membrane increased to 93.65% and 66.74% respectively, while those of the original one were 72.82% and 31.72%. Moreover, the irreversible pollution rate decreased by 55%. The most notable effect was, when going through four consecutive antimicrobial tests with the contacting time 2 h at 38 °C, the antimicrobial rates of the membrane were 92.3%, 88.5%, 87.9% and 85.6%, respectively, which can effectively prevent the modified membrane from biological fouling, while the original membrane did not have any antimicrobial behaviors.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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