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# Surface properties and interception behaviors of GO-$TiO_2$ modified PVDF hollow fiber membrane

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**Abstract.** To investigate surface properties and interception performances of the new modified PVDF membrane coated with Graphene Oxide (GO) and nano-$TiO_2$ (for short the modified membrane) via the interface polymerization method combined with the pumping suction filtration way, filtration experiments of the modified membrane on Humic Acid (HA) were conducted. Results showed that the contact angle (characterizing the hydrophilicity) of the modified membrane decreased from 80.6±1.8° to 38.6±1.2°. The F element of PVDF membrane surface decreased from 60.91% to 17.79% after covered with GO and $TiO_2$. O/C element mass ratio has a fivefold increase, the percentage of O element on the modified membrane surface increased from 3.83 wt% to 20.87%. The modified membrane surface was packed with hydrophilic polar groups (like -COOH, -OH, C-O, C=O, N-H) and a functional hydrophilic GO-polyamide-$TiO_2$ composite configuration. This configuration provided a rigid network structure for the firm attachment of GO and $TiO_2$ on the surface of the membrane and for a higher flux as well. The total flux attenuation rate of the modified membrane decreased to 35.6% while 51.2% for the original one. The irreversible attenuation rate has dropped 71%. The static interception amount of HA on the modified membrane was 158.6 mg/$m^2$, a half of that of the original one (295.0 mg/$m^2$). The flux recovery rate was increased by 50%. The interception rate of the modified membrane on HA increased by 12% approximately and its filtration cycle was 2-3 times of that of the original membrane.

**Keywords:** GO-$TiO_2$ modified PVDF membrane; hydrophilicity; the flux attenuation rate; antifouling performance; interception behaviors

## 1. Introduction

In recent years, water pollution has become a severe problem in China. Micro-pollutants, especially dissolved organics and nutrients with low molecular weights, are not easily removed via conventional water treatment processes (coagulation-sedimentation -filtration-disinfection) (Loo *et al*. 2012, Wang *et al*. 2013). Under such situation, membrane treatment technology is becoming more and more popular, especially for the ultrafiltration membrane technology, which has been used in water treatment widely. Amongst raw materials for preparing ultrafiltration membrane, polyvinylidene fluoride (PVDF) has become one of the most popular membrane materials due to its great amount of advantages, like good chemical stability, highly mechanical strength and anti-aging property (Chen 2016). However, PVDF with strong hydrophobicity is highly susceptible to membrane fouling, resulting in a sharp decrease in membrane flux and a significant reduction in the length of service, which limits its extensive popularization and application. The hydrophilic modification of PVDF membrane can effectively improve its anti-fouling performance and interception capacity (Du *et al*. 2009, Sarihan and Eren 2017, Sathish *et al*. 2015).

At present, PVDF membrane hydrophilic modification falls into two categories: blending modification and surface modification. The blending modification method has the advantages of long lasting effect of the modifying agent, easy operation and so on. However, there are disadvantages that the hydrophilic performance is limited and the modifying agent is difficult to disperse. In addition, the physical and chemical properties of the membrane via blending modification change easily and are difficult to control. Surface modification significantly improves hydrophilic effect, and will not affect the physical and chemical properties of the original membrane, but there are also issues that the modifying agent is easy to fall off, surface grafting process is too complex and difficult to control and the hydrophilic surface structure formed by the interface polymerization process is of limited hydrophilic abilities and etc.

Therefore, this paper introduces a new modified PVDF membrane being made in the laboratory (Guangdong University of Technology, China) through an easy operational method of interfacial polymerization and pumping suction filtration. The highly hydrophilic nanomaterials—Graphene Oxide (GO) and Titanium Dioxide ($TiO_2$) were employed as the modifying agents and their combined advantages after being coated on the surface of the original PVDF membrane were studied. This paper would investigate the surface performances (like hydrophilicity, interception behaviors, removal rate,

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antifouling performance) of the GO-$TiO_2$ modified membrane against micro-pollutant of HA.

## 2. Material and methods

### 2.1 Materials

PVDF hollow fiber ultrafiltration membrane module, with the largest pore size of 0.01 μm, the inner diameter of the membrane fiber of 0.8 mm, the outer diameter of 1 mm, the number of the membrane fibres of 212, length of 15 cm, and membrane area of 0.200 $m^2$, was purchased from Hangzhou Mai'na Membrane Technology Co. Ltd.. Graphene Oxide (GO), with thickness of 0.8-1.2 nm, purity of 99 wt% (mass percentage concentration), was purchased from Nanjing Xianfeng Nano-materials Technology Co. Ltd.. Cetyl trimethyl ammonium bromide (CTAB, molecular weight: 364.5), tetrabutyl orthotitanate (TBOT, molecular weight: 340.3), hydrochloric acid (HCl, molecular weight: 36.5), n-hexane (molecular weight: 86.2), absolute ethyl alcohol (molecular weight: 46.1) were all analytically pure, and purchased from Tianjin Daming Chemical Reagent Factory. M-phenylenediamine (MPD, molecular weight: 108.1), trimesic acid chloride (TMC, molecular weight: 265.5), humic acid (HA, fulvic acid FA > 90%, average molecular weight: Mn=1032), were all analytically pure, and purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.

### 2.2 Preparation of GO-$TiO_2$ mixed dispersion

Nano-$TiO_2$ dispersion was prepared by sol-gel method. At first, drop butyl titanate ethanol solution into stirred HCl solution (pH=3, stirring strength=800 r/min) slowly, with the volume ratio of butyl titanate: anhydrous ethanol: water = 1:10:90. Next, stir the mixed solution violently for 6 hours (stirring strength=800 r/min). Then put it into an ultrasonic cleaner for 5 min (ultrasonic power=150 W) and $TiO_2$ dispersions were prepared. Afterwards, a certain amount of 100 mg/L GO dispersion was added to the $TiO_2$ dispersant gradually, and the volume was fixed to 500 mL with HCl solution (pH=3). Finally, the dispersion of GO and $TiO_2$ was prepared after ultrasonic oscillation for 15 min.

### 2.3 GO-$TiO_2$ modified membrane preparation procedure

First of all, the original PVDF membrane module was immersed in CTAB solution (1 g/L) for 10 min. CTAB is an amphiphilic cationic surfactant with both hydrophilic and hydrophobic ends, which was employed to conduct the pretreatment of the membrane surface to enhance its surface activity. The activated membrane surface bonded with highly hydrophilic substances much more tightly. The details were reported in the document of You (You *et al*. 2012). Then, the prepared GO-$TiO_2$ mixed dispersion liquid was filtered through the membrane module by the peristaltic pump (YZ1515X type, Baoding) under the pressure of 0.04 Mpa. Excess 5 min of pumping was needed after the solution is out and dry the module in a drying oven (KLG-9020 type, Shanghai) at 60°C for 30 min. Afterwards, it was immersed in the MPD solution (1 wt%, dissolved in water) for 8 min. After soaking, the peristaltic pump was used to dry the rest of water on the membrane fibers. Finally, it was immersed in the TMC oil phase solution (0.2 wt%, dissolved in n-hexane) for 10 min to conduct the interfacial polymerization process. After drying, the homemade GO-$TiO_2$ modified membrane was ready.

### 2.4 Surface properties characterization of GO-$TiO_2$ modified membrane

#### 2.4.1 GO-$TiO_2$ modified membrane surface characteristics

The surface properties of the GO-$TiO_2$ modified membrane were presented by testing the following parameters: static contact angle, functional groups, elemental content and composition on the surface, appearance characteristics and etc. The GO-$TiO_2$ modified membrane module was immersed in 30%, 50%, 70% and 100% absolute ethyl alcohol successively for 30min respectively, then it was dried in a drying oven at 60°C. Afterwards, the surface contact angle tester (HARKE-SPCA type, Beijing), scanning electron microscopy (SEM, JEM-2100 type, Japan) and its supporting X-ray energy spectrum analyzer and Fourier infrared spectrometer (Nicolet6700, American Thermofisher Corporation) were used to test the surface characteristic parameters mentioned above.

#### 2.4.2 The flux test of GO-$TiO_2$ modified membrane

The peristaltic pump was used under a suction pressure of 0.08 MPa to provide transmembrane pressure in the process of membrane operation. After the membrane module was running steadily, the pure water flux (J) was tested.

Then, the pure water was replaced with HA solution (100 mg/L). The water flux was tested after GO-$TiO_2$ modified membrane trapped HA solution for 10 hour. Then, the GO-$TiO_2$ modified membrane was cleansed by clean water (hydraulic cleansing pressure and time were 0.04 MPa and 15 min separately). After the backwashing, the measurement of the pure water flux through GO-$TiO_2$ modified membrane was done. The total attenuation rate, the reversible attenuation rate and the irreversible attenuation rate would be obtained from the Eqs. (1)-(3).

$$R_t=\frac{J_{w1}-J_{HA}}{J_{w1}}\times 100\% \quad (1)$$

$$R_r=\frac{J_{w2}-J_{HA}}{J_{w1}}\times 100\% \quad (2)$$

$$R_{ir}=R_t-R_r \quad (3)$$

Where $R_t$, $R_r$ and $R_{ir}$ represented the total attenuation rate, the reversible attenuation rate and the irreversible attenuation rate respectively, and $J_{w1}$, $J_{HA}$ and $J_{w2}$ were the initial pure water flux through the clean modified membrane, the water flux through modified membrane after trapping HA solution for 10 hour, and pure water flux

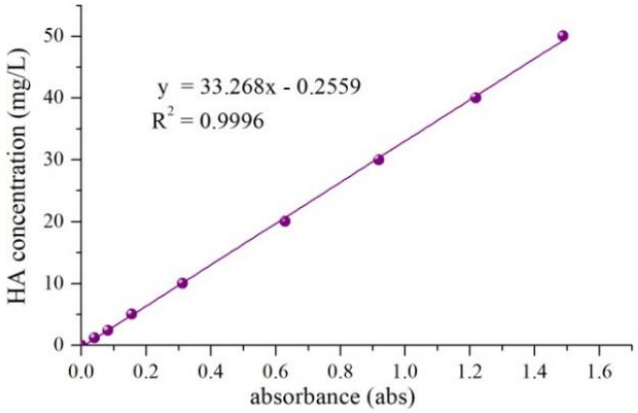



Fig. 1 the standard curve – the relationship between HA concentration and absorbance

through modified membrane after hydraulic cleansing separately, units of the water flux are all $L/m^2 \cdot h$.

#### *2.4.3 Static adsorption capacity of GO-TiO2 modified membrane trapping HA*

The easier the organic matter being adsorbed to the membrane surface, the more the membrane being determined by fouling (Sarihan and Eren 2017). The GO-$TiO_2$ modified membrane fibers, whose effective membrane area was 10 $cm^2$, was tied by strings at both ends. Then the prepared membrane fibers were immersed in HA solution (10 mg/L) for 24 hour. According to the difference of HA concentration before and after soaking, the amount of HA adsorbed on the surface of GO-$TiO_2$ modified membrane module was determined.

#### *2.4.4 The test of flux and interception rate of GO-TiO2 modified membrane trapping HA and its antifouling performance*

The interception rate was used to characterize the ability of GO-$TiO_2$ modified membranes trapping organic matters in micro-polluted raw water. First, the prepared HA solution (10 mg/L) was filtered through GO-$TiO_2$ modified membrane. After 30 min, the filtered water was sampled, and the measurement of the absorbance of the water sample was conducted by UV spectrophotometer (UV759, Beijing). The standard curve was drawn to show the relationship between the HA concentration and the absorbance (see Fig. 1). According to the standard curve and the measured absorbance of water sample, the remainder concentration of HA remained in water sample was calculated. Afterwards, the HA interception rate (η) was obtained.

The antifouling performance of the GO-$TiO_2$ modified membrane module was demonstrated by measuring the change of water flux with the filtration time in the process of GO-$TiO_2$ modified membrane module trapping HA in specific filtration period. This measurement was performed under the suction pressure of 0.08 Mpa (provided by peristaltic pump), with HA solution of 100 mg/L.

When the filtration period was 0-600 min, the interception efficiency of GO-$TiO_2$ modified membrane trapping HA was obtained. When discussed the influence of hydraulic cleansing on the change of water flux with the filtration time in the process of GO-$TiO_2$ modified membrane module trapping HA, the filtration period was changed into 0-300min. In addition, a hydraulic cleansing (the pressure and time were 0.04 Mpa and 15 min separately) was added every time the filtration ended. After the process of "filtering- hydraulic cleansing" was repeated for 5 times, the impact was investigated.

## 3. Results and discussions

### *3.1 The comparison of the membrane performances under different preparation conditions*

PVDF membranes modified with GO or $TiO_2$ solely were compared to prove the synergistic effect between GO and $TiO_2$ which shown in Table 1. After the membrane being coated with the modifying agents, the pure water flux decreased because of the pore size of the membrane was reduced. The HA adsorbance difference of the modified membrane under different conditions were very clear. Their adsorption capacity was ranked as: suction filtration adsorption with GO modifying agents (289 $mg/m^2$) > suction filtration adsorption with $TiO_2$ modifying agents (273 $mg/m^2$) > suction filtration adsorption with GO-$TiO_2$ modifying agents (265 $mg/m^2$) > interfacial polymerization (220 $mg/m^2$) > suction filtration adsorption with $TiO_2$ modifying agents + interfacial polymerization (185.5 $mg/m^2$) > suction filtration adsorption with GO modifying agents + Interfacial polymerization (142.7 $mg/m^2$) > suction filtration adsorption with GO-$TiO_2$ modifying agents + interfacial polymerization (108 $mg/m^2$).

A higher adsorption capacity means a lower antifouling ability. Hence, the priority of the modification way is the combination of suction filtration with interfacial polymerization, then followed interfacial polymerization, the last one is suction filtration adsorption. Suction filtration adsorption is a physical modification way, the modifying agents is easy to fall off from the membrane surface which presents a lower interception rate of HA (see Table 1). Interfacial polymerization involves chemical grafting, and the polyamide coating formed by interfacial polymerization is tightly bound to the surface of the membrane.

For the modifying agents, the combination of GO with $TiO_2$ under different conditions has demonstrated higher interception rate than only GO or $TiO_2$ has presented. The synergistic effect of PVDF membranes modified with GO and $TiO_2$ has been proved much higher than that GO or $TiO_2$ solely. The hydrophilicity of GO or $TiO_2$ is much better than that of polyamide, so the anti-fouling property of modified membrane can be further improved. When GO and $TiO_2$ are combined, the gap between GO layers can be filled with $TiO_2$. These two nano-materials can be spacer to isolate each other and the nanohybrids exhibit remarkable synergistic interactions (Pan *et al*. 2015, 2016, 2018). The anti-fouling performance of the GO- $TiO_2$ modified membrane is obviously better than that of the single modifying agents.

The optimal modification way, suction filtration adsorption with GO-$TiO_2$ modifying agents combined with interfacial polymerization, offered the highest interception rate (91%) and lowest HA adsorbance (108 $mg/m^2$) which

Table 1 The comparison of the membrane performances under different preparation conditions

| Membrane under different preparation conditions | GO | $TiO_2$ | suction filtration adsorption | Interfacial polymerizetion | HA adsorbance ($mg/m^2$) | Pure water flux($L/m^2 \cdot h$) | HA Interception rate(%) |
|---|---|---|---|---|---|---|---|
| clean without any modification | ×** | × | × | × | 295 | 56.2 | 81 |
| suction filtration adsorption modification with GO modifying agents | √* | × | √ | × | 289 | 56.1 | 80.5 |
| suction filtration adsorption modification with $TiO_2$ modifying agents | × | √ | √ | × | 273 | 55.2 | 82.5 |
| Interfacial polymerization modification | × | × | × | √ | 220 | 50.1 | 85.5 |
| suction filtration adsorption modification with GO-$TiO_2$ modifying agents | √ | √ | √ | × | 265 | 55.6 | 86.2 |
| suction filtration adsorption modification with GO modifying agents + Interfacial polymerization modification | √ | × | √ | √ | 142.7 | 52.7 | 87.4 |
| suction filtration adsorption modification with $TiO_2$ modifying agents + Interfacial polymerization modification | × | √ | √ | √ | 185.5 | 53.1 | 87.1 |
| suction filtration adsorption modification with GO-$TiO_2$ modifying agents +Interfacial polymerization modification | √ | √ | √ | √ | 108 | 54.4 | 90.1 |

*√: the modifying agents was added or the modification was processed; **×: the opposite to √

revealed the desirable surface behaviors of the GO-$TiO_2$ modified PVDF membrane.

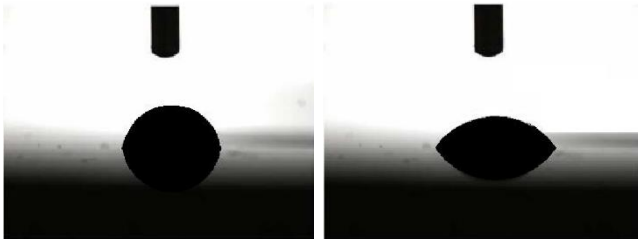
### *3.2 Hydrophilic properties and antifouling performances analysis of GO-$TiO_2$ modified membrane*

#### *3.2.1 Static contact angle*

Static contact angle is the most frequently used index for characterizing membrane hydrophilic properties. A highly hydrophilic ultrafiltration membrane has a small static contact angle. Meanwhile, good hydrophilic performance reflects good antifouling performance (Aryanti *et al*. 2015, Subasi and Cicek 2017). The static contact angle of GO-$TiO_2$ modified surface was decreased by 52.2% of that of the original one. It was 80.6±1.8° (see Fig. 2(a)) for the original one while 38.6±1.8° (see Fig. 2(b)) for the modified one after introducing the highly hydrophilic GO and $TiO_2$ as the modifying agents. It indicated that the hydrophilicity of the membrane was enhanced. In addition, the result of the static adsorption experiment revealed that the static adsorption amount of the modified membrane on HA decreased from 295.0 mg/m2 to 158.6 mg/m2, which was a half of that of the original one. It indirectly indicated that antifouling performance of GO- $TiO_2$ modified membrane was greatly improved as well. Therefore, lower static contact angle and static adsorption amount can illustrate the hydrophilic property and antifouling performance of GO- $TiO_2$ modified membrane at the same time.

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

The infrared spectra characteristics of the original membrane, GO- $TiO_2$ modified membrane and GO were analyzed according to the measuring results (see Fig. 3). It was very clear that the nano-modifying agents GO and $TiO_2$ have contributed a great many polar groups attached on the surface of the modified membrane firmly, like -CH, -OH,



(a) the original membrane (80.6±1.8°) (b) the modified membrane (38.6±1.8°)

Fig. 2 The comparison of the static contact angle of the original membrane with that of the modified one by HARKE - SPCA series contact angle measurement

C=O and C-O. Therefore, the hydrophilic nature and the antifouling performance were improved significantly.

The details and characteristics of the polar groups and the vibration adsorption peak were illustrated as below according to Fig. 3. The position near 2928 cm-1 and 2949 cm-1 corresponded to the vibration adsorption peak of the hydrocarbon bond (-CH); the stretch vibration adsorption peak of the hydroxyl groups (-OH) was in line with the position of 3380 cm-1; in addition, 1728 cm-1, 1621 cm-1, 1053 cm-1 and 1173 cm-1 corresponded to the vibration adsorption peak of the carbonyl group (C=O), carbon-carbon double bonds (C=C), Epoxy bond (C-O) and the C-F bond in PVDF materials (C-F). All were in agreement with reports in the related literature (Wang *et al*. 2015, Wu *et al*. 2008, Zaaba *et al*. 2017, Zheng *et al*. 2011).

Compared with the original membrane in Fig. 3(a), the GO-$TiO_2$ modified membrane in Fig. 3(b) showed strong vibration adsorption peaks at 3380 cm-1 (corresponding to -OH bond) and 1053 cm-1 (C-O bond); strengths of vibration peaks at 1728 cm-1and 1621 cm-1 were both enhanced. This proved that GO introduced a great many polar groups such as OH, C-O and C=O to the surface of

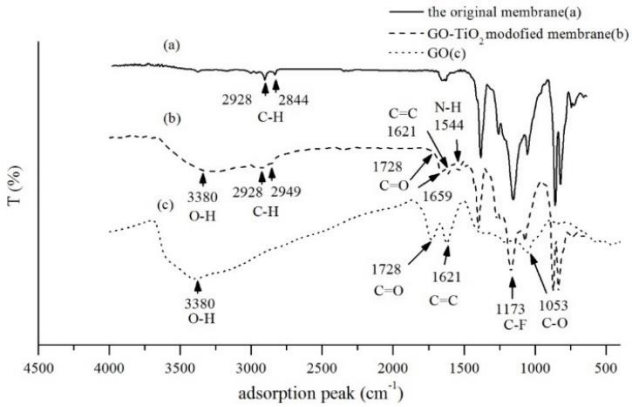



Fig. 3 Analysis of original membrane, GO-$TiO_2$ modified membrane and GO by FTIR

the modified membrane. However, Fig. 3(b) also revealed another two strong stretch adsorption vibration peaks in amide II at 1544 cm-1 and in amide I at 1659 cm-1, corresponding to N-H bond and C=O bond respectively. The existence of these two peaks proved that there was a layer of polyamide cortex on the surface of GO-$TiO_2$ modified membrane (Shawky 2011, Tarboush *et al*. 2008). Hence, some of the hydrophilic properties were contributed by N-H and C=O in the polyamide cortex. The coating and wrapping effect of polyamide cortex generated by interfacial reaction improved the adhesion firmness of the two modifying agents (GO and $TiO_2$) on the surface of membrane. The highly hydrophilic properties of GO and $TiO_2$ encouraged the modified membrane showing better surface properties than the original PVDF membrane

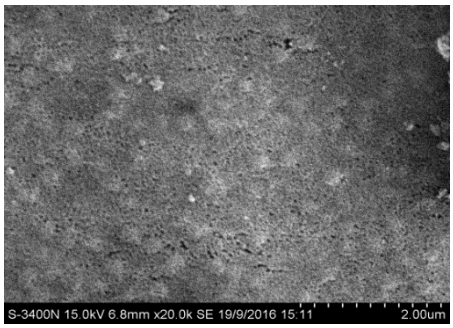
### *3.2.3 Morphological features and elemental spectrum analysis on the surface of GO-$TiO_2$ modified membrane*

The morphological features on the surface of the original membrane and the GO- $TiO_2$ modified one were revealed by scanning electron microscopy (SEM) photos (see Figs. 4(a)-(b)). The original membrane surface was relatively smooth and uniform in pore size distribution (see Fig. 4(a)). Compared with the original membrane, the surface appearance and structures of the modified one has become more rough and complicated. The upper and lower ridge of the modified membrane was ladder-shaped, its layers scattered with each other, and the surface of the membrane had a flaky and sharp edge structure (see Fig. 4(b)).

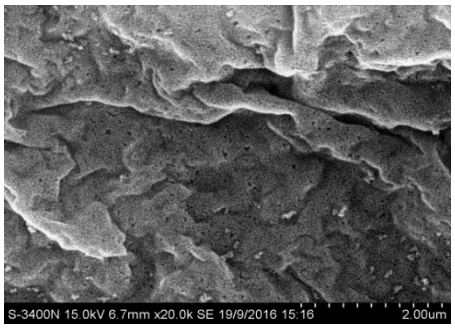
The very thin layers with sharp edges were GO sheet layers which was similar to the GO structures reported by Choi *et al*. (2013). The other part of membrane surface which was far away from the sharp edge was the polyamide cortex layer generated by interface polymerization. The size of GO sheet layer was larger, so a part of it was embedded in the polyamide layer. When GO sheet layer was not completely covered, it solidly bonded with the polyamide coating and was not easy to fall off. At the same time, on the surface of the GO-$TiO_2$ modified membrane, we couldn't see a large amount of $TiO_2$ particles (see Fig. 4(b)), possibly due to the fact that the $TiO_2$ particles were relatively small compared with the GO and were hidden under both GO sheet layer and polyamide layer. In addition to the structure of the sharp edges, the modified membrane also contained a large number of membrane pores on its surface (see Fig. 4(b)) compared with the original one (see Fig. 4(a)). The sectional profile features of the original membrane and the modified one were very similar (as shown in Figs. 4(c)-(d)). This indicated that the membrane modification only affected the surface appearance and did not alter the inner structures of the original membrane.

The elemental content and composition on the surface of the modified membrane were analyzed by Energy Dispersive Spectroscopy (EDS), which was shown in Fig. 5. The content of the element F contained in the surface of GO- $TiO_2$ modified membrane was 17.79% while it was 60.91% before modification. The F element in the original membrane was derived from the membrane material PVDF itself. After modification, the F element of the membrane surface decreased so obviously that the surface of the modified membrane was shown to having almost been covered with the hydrophilic functional layer. The changes in the content of the element C and O were also very clear. The mass ratio of the element O to the element C increased to 0.556 from 0.109 before the modification, resulted in the greatly improved hydrophilicity on the surface. The mass percentage of the element O contained in the modified membrane surface increased from 3.83% to 20.87%, which was mainly from three sources contributing element O, including $TiO_2$, GO which was rich in -OH and -COOH and other hydrophilic oxygen-containing functional groups, and the polyamide cortex where contained C=O functional groups. In addition, according to the Figs. 3-4, some important information can be revealed here: in the uppermost layer of the membrane surface was the polyamide cortex, followed by a GO sheet embedded in the surface of the polyamide cortex, and then $TiO_2$ was under the GO layer and the polyamide cortex. Therefore, the hydrophilicity of GO- $TiO_2$ modified membrane surface has been improved because the combination of the polyamide cortex, the GO layer and $TiO_2$ mentioned above constituted a hydrophilic surface of GO- $TiO_2$ modified membrane. The simple use of GO and $TiO_2$ to modify the surface of the membrane easily leads to the loss of the hydrophilic functional layer on the surface of the modified membrane. The interface polymerization being used in the preparation experiments belonged to chemical grafting. The polyamide cortex generated by the interface polymerization can be firmly adhered to the surface of the modified membrane. However, the hydrophilicity of the polyamide cortex itself was insufficient, and the anti-fouling property improvement of the modified membrane by taking the interface polymerization alone was limited. The combination of interface polymerization reaction with GO and $TiO_2$ improved the antifouling performance of the surface of the original film to a great extent.

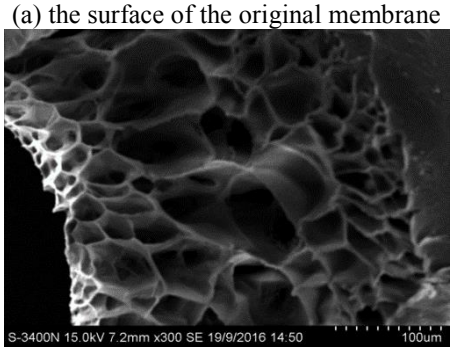
The two modifying agents (GO and $TiO_2$), the polyamide coating layer, and the PVDF membrane interact with each other. First, $TiO_2$ particles have strong adhesion and can fill the gap between GO and the original membrane, thereby enhancing the adhesion of GO on the membrane surface. Then the two nano-materials can be spacer to isolate each other and the nanohybrids exhibit remarkable synergistic interactions (Pan *et al*. 2015, 2016, 2018). After the interfacial polymerization was conducted



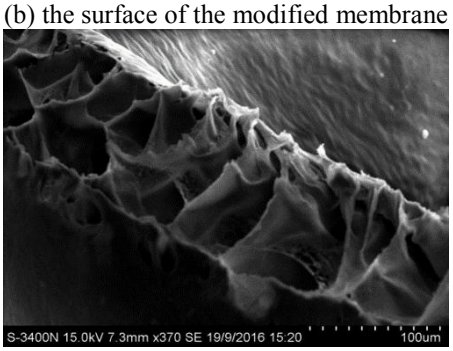

(a) the surface of the original membrane




(b) the surface of the modified membrane

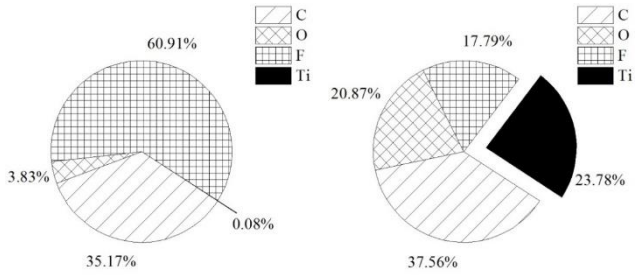



(c) the section of the original membrane




(d) the section of the modified membrane

Fig. 4 The comparison of morphological structures of SEM photos of the GO-$TiO_2$ modified membrane and the original one




(a) the GO-$TiO_2$ modified membrane (b) the original membrane

Fig. 5 The mass percentage (%) of each element packed on the surface of the original membrane and modified membrane via the energy spectrum analysis method

by immersing in MPD and TMC, the polyamide cortex layer formed by polymerization is bound to the surface of the membrane tightly. The polyamide coating layer improved the GO and $TiO_2$ firmness on the surface membrane, made full use of GO and $TiO_2$ excellent hydrophilic properties, as well as making the modified membrane show strong antifouling ability compared with the original membrane. In addition, Polyamide coating layer also has a certain hydrophilicity, so it can greatly improve the anti-fouling performance of the modified membrane.

### *3.3 The interception behaviors of GO-$TiO_2$ modified membrane*

#### *3.3.1 The membrane flux and attenuation rate analysis and its antifouling abilities*

The flux attenuation rate indicates the antifouling ability of the modified membrane indirectly. Compared with the original membrane, the modified one demonstrated better membrane flux as well as antifouling ability after trapping HA and hydraulic cleansing, which was shown in Table 2. Not only did the total attenuation rate of the modified membrane flux decline to 35.6% (51.2% for the original one), its irreversible attenuation rate decreased obviously as well, which was from 24.3% (the original one) to 7.1% (the modified one). This indicated that the antifouling ability of the modified membrane was remarkably improved. The possible reasons were listed below. First of all, the polyamide layer on the outer surface of the membrane partly covered a part of the GO sheet layer to possibly prevent its falling off. Secondly, since the hydrophilic property of GO itself was strong, a protective layer of the hydrated shell was formed on the surface of the GO sheet layer, to prevent the emergence of stripping off caused by shear force during hydraulic cleansing. In addition, $TiO_2$ particles have strong adhesion (Tavakol moghadam *et al*. 2016), and can fill the gap between GO and the original membrane, thereby it enhanced the adhesion of GO on the membrane surface (see Fig. 6). Therefore, the improved hydrophilicity and smaller pore size of the modified membrane surface led to a higher HA retention rate (92.1%), while the original one had only 80.5% of retention rate on HA.

Seen from Fig. 6, the antifouling behavior was enhanced significantly. After the GO- $TiO_2$ modified membrane undergoing 5 consecutive "filtering - hydraulic cleansing" cycles, the membrane flux can be steadily above 48 L/$m^2$·h (51 L/$m^2$·h under its original clean situation). Its flux recovery rate was up to 94%. However, the original membrane flux was only 36.8 L/$m^2$·h after 5 cycles, which had the flux recovery rate of only 69% compared with the flux of the original clean one (53.3 L/$m^2$·h). Therefore,

Table 2 The comparison of performance parameters between the GO-$TiO_2$ modified membrane and the original membrane

| membrane | water flux $J_{w1}$ (L/m²·h) | water flux after trapping HA $J_{HA}$ (L/m²·h) | water flux after hydraulic cleansing $J_{w2}$ (L/m²·h) | the total attenuation rate of membrane flux $R_t$ (%) | reversible attenuation rate $R_r$ (%) | irreversible attenuation rate $R_{ir}$ (%) | HA retention rate (%) |
|---|---|---|---|---|---|---|---|
| the modified | 54.4 | 35.0 | 50.5 | 35.6 | 28.5 | 7.1 | 92.1 |
| the original | 56.2 | 27.4 | 42.5 | 51.2 | 26.9 | 24.3 | 80.5 |

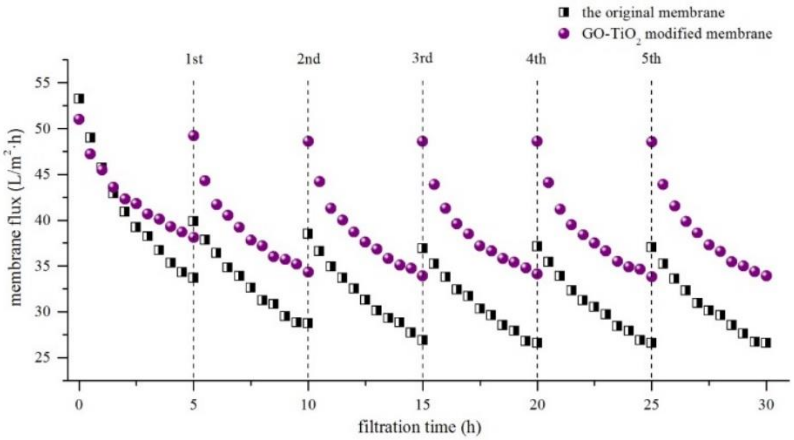



Fig. 6 The variation of water flux with filtration time in the process of the original and modified membranes trapping HA before and after hydraulic cleansing

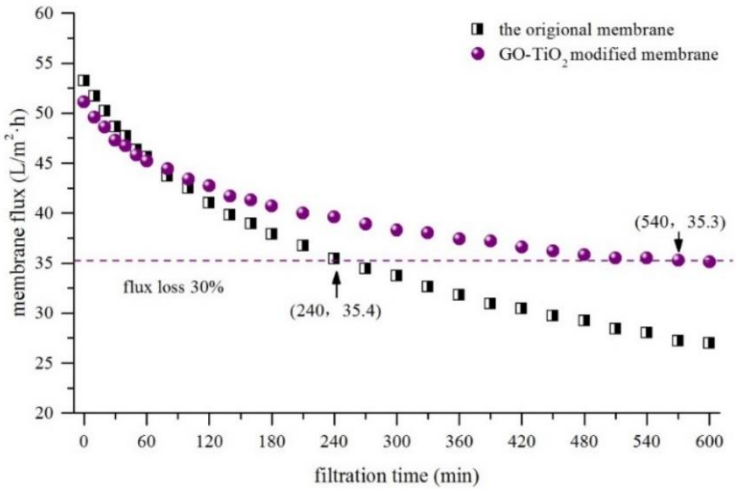



Fig. 7 The water flux varies with filtration time in the process of the original and modified membranes trapping HA

GO- $TiO_2$ modified membrane was resistant to highly frequency cleansing, and its flux recovery rate was high too. The hydraulic cleansing can effectively remove the contaminants from the surface of the GO- $TiO_2$ modified membrane without damaging the hydrophilic coating layers with nano-pores, which was contributed to the highly antifouling performance.

### *3.3.2 The interception efficiency of GO-$TiO_2$ modified membrane trapping HA*

The change of the water flux with filtration time in the process of the original and modified membranes trapping HA was demonstrated in Fig. 7. It was obvious that the filtration cycle of GO-$TiO_2$ modified membrane were remarkably prolonged. The water flux of the original membrane decreases with the filtration time rapidly, while the decreasing trend of the modified membrane filtration curve was more stable. When the water flux of the modified membrane was lost by 30%, the filtration time of the HA solution passing through the modified membrane increased by 2.25 times of that of the original one (from 240 min before modification to 540 min after modification).

## 4. Conclusions

The combination of the polyamide cortex, the GO layer and $TiO_2$ constituted a hydrophilic surface of GO-$TiO_2$ modified membrane. The hydrophilic functional layer of the GO-$TiO_2$ modified PVDF membrane was of GO-

polyamide-$TiO_2$ composite structure. It provided a rigid network structure for the GO and $TiO_2$ being attached on the surface of membrane tightly. The F element of PVDF membrane surface decreased from 60.91% to 17.79% after covered with GO and $TiO_2$. O/C element mass ratio has a fivefold increase, the percentage of O element on the modified membrane surface increased from 3.83 wt% to 20.87%.

The hydrophilicity of the GO-$TiO_2$ modified PVDF membrane was improved significantly. The surface of GO-$TiO_2$ modified membrane was rich in a lot of hydrophilic polar functional groups such as -OH, C-O, C=O, N-H and so on. The contact angle of the modified membrane was decreased to 50% of that of the original one. The static adsorption amount of the modified membrane on HA decreased to 158.6 mg/m$^2$ which was half of that of the original one (295.0 mg/m$^2$).

The flux attenuation rate and the antifouling ability of the modified membrane were enhanced dramatically. The total flux attenuation rate of the modified membrane decreased from 51.2% to 35.6%. In particular, the irreversible attenuation rate has dropped 71%, which decreased from 24.3% to 7.1%. The flux recovery rate of GO-$TiO_2$ modified membrane can still reach 94% at the initial filtration time while the original membrane can only reach 69% at the initial moment of filtration.

The separation and interception behaviors of the GO-$TiO_2$ modified membrane were enhanced markedly. Its interception rate of GO-$TiO_2$ modified membrane on HA increased from 80.5% to 92.1%. The filtration cycle of the modified PVDF membrane was lengthened by 2-3 times of that of the original one.

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